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Synthesis of a new stable and water-soluble tris(4-hydroxysulfonyl-tetrachlorophenyl)methyl radical with selective oxidative capacity

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ABSTRACT

A new stable organic free radical of the PTM (perchlorotriphenylmethyl) series very soluble in water is reported. This free radical is sensitive to electron transfer processes, and the selectivity of these reactions in the presence of ascorbic acid, pyrogallol, and catechol as reducing species is described. The electron paramagnetic resonance spectrum and the electrochemical behavior are also presented.

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1. Introduction

We have been engaged for a time with the synthesis of organic radicals of the TTM¹ ((2,4,6-trichlorotriphenyl)methyl) and PTM² ((perchlorotriphenyl)methyl) series very stable, both in solid and in solution, yet very active in redox processes reacting with electron-donating substrates by electron transfer reactions. In this context, strongly oxidant radicals, such as HNTTM³ and TNPTM⁴ radicals (Scheme 1) have been prepared and assayed as chemosensors of the antioxidant power of many natural and synthetic polyphenols. Zhou et al. have recently reported the radical-scavenging ability of some resveratrol derivatives against HNTTM radical.⁵ The results obtained indicate that the oxidative capacity of these radical species is intimately related to their electrochemical behavior, a high reduction potential being indicative of a high oxidant power of the radical. In this way, HNTTM radical with a high cathodic peak potential ($E_p^c = 0.50 \text{ V}$) is capable of oxidizing catechol (1,2-dihydroxybenzene) and pyrogallol (1,2,3-trihydroxybenzene),^{3f} and those natural antioxidants, which contain these polyphenols as part of their molecular structures.^{3c,e} TNPTM radical, with lower cathodic peak potential ($E_n^c = 0.14 \text{ V}$) is able to discriminate between the antioxidant activities of both polyphenols, being only active with pyrogallol.^{4a} In summary, the

more positive the potential of reduction of the radical, the more active is with antioxidants. By using both radicals, useful information about total electron transfer capacity of phenolic scavengers and the presence of highly reactive positions can be obtained. Unfortunately, these chemosensors cannot be used in experiments that require water as a solvent because of their hydrophobicity.



Herein, we report the synthesis, characterization, and redox reactions of a new stable and water-soluble radical of the PTM series with acidic sulfonic groups in *para*-position, the TSPTM radical (1).





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2. Results and discussion

2.1. Synthesis and properties

The experimental method to prepare this radical is displayed in the Scheme 2 and consists of a three-step mechanism. A Friedel-Crafts reaction between an excess of 1.2.4.5-tetrachlorobenzene and chloroform in the presence of aluminum chloride as a Lewis acid at 160 °C in a glass pressure vessel resulted in the formation of tris(2,3,5,6-tetrachlorophenyl)methane with an excellent yield.⁶ The para-positions were then sulfonated with fuming sulfuric acid (SO₃, 60%) to give the trisulfonic acid α *H*-TSPTM (**2**) also with excellent yield. α *H*-TSPTM (**2**) is very soluble in neutral H₂O where the sulfonic groups are completely ionized producing a trianion. The solutions of 2 in water are strongly acid (160 μ M, pH ~ 3.4). Under these conditions, the central carbon atom remains completely associated, and it is so weakly acid that it is not dissociated in saturated sodium bicarbonate solutions (pH \sim 8.2) and even in a basic buffer solution (pH \sim 10.2), as confirmed by UV-vis spectroscopy.



The acid dissociation constant, $pK_{HA} \sim 13.1$, of the saturated carbon atom in **2** has been calculated from its colored basic aqueous solutions by UV–vis spectroscopy (Scheme 3).⁷ Values of the pK_{HA} provide a fundamental data base for assessment of the electronic and steric effects in organic molecules. The very large value found in **2** is a consequence of both effects. The electronic effect produced by the presence of three negative charges of the sulfonate groups in *para*-position inhibits drastically the dissociation of the C–H bond. In addition, the charge delocalization of the conjugate base C^{Θ} on adjacent phenyl rings is sterically diminished because the presence of six *ortho* chlorine atoms induces a twist of the phenyl rings, the molecule adopting a propeller conformation.⁸



Scheme 3.

Due to the strong acidic *para*-sulfonic groups in the molecule, a new methodology, different from that used in the radicals of the PTM series,^{2a} has been employed to generate the radical species from **2**. When α *H*-TSPTM in THF/H₂O was treated with an excess of KOH (2 M), the solution evolved to a strong red color. Then, a small excess of *para*-chloranil in solid was added to yield the trianion of the TSPTM radical that in methanol and with an ion exchange resin afforded TSPTM radical in a nearly quantitative yield. Similar to compound **2**, the radical **1** is also very soluble in water. Aqueous solutions of **1** are also very acidic (pH ~ 3.5 at ~ 1×10^{-4} M). Radical **1** is very stable either as solid or in aqueous solution (it is recovered in 94% after 24 h in the air) and can be stored in solid at low temperature without any observable decomposition.⁹

The UV—vis absorption spectrum of the TSPTM trianion radical in aqueous solution is characterized by two bands associated with its radical character (Fig. 1). The high-energy band corresponds to a transition from the SOMO orbital to the LUMO [$\lambda(\varepsilon)$, 385 (17,280 L mol⁻¹ cm⁻¹) nm] and the weak and low energy band showing some fine structure in the visible region [$\lambda(\varepsilon)$, 503 (740) and 556 (sh) (615)] involves the promotion of one electron from the HOMO to the SOMO. As the unpaired electron is mainly located on the trivalent carbon atom, the atomic orbital 2p might have a major contribution in the SOMO orbital. The absorption spectrum of a tetraanion generated either by deprotonation of the α *H*-TSPTM in a strongly basic degassed aqueous solution or by reduction of the TSPTM radical also in degassed aqueous KOH solution, presents one broad band [$\lambda(\varepsilon)$, 535 (10,630)], typical of these charged species. This tetraanion is stable in basic solutions in the dark for hours.



Fig. 1. UV–vis spectra of (a) TSPTM trianion radical in water, $(a \times 10)$ a detail of the multiplet of the lowest energy band with values given in the text, and (b) TSPTM tetraanion generated from TSPTM trianion radical in KOH (2 M).

X-band electron paramagnetic resonance (EPR) spectrum of TSPTM trianion radical was recorded in aqueous solution $(\sim 10^{-3} \text{ M})$ at room temperature and showed a single and narrow Lorentzian band (g=2.0022 \pm 0.00003; linewidth, ΔH_{pp} =0.7 G) (Fig. 2). At higher gain values, the isotropic coupling with the 13 C nuclear spins of the α -carbon atom, the three bridgehead carbon atoms, and the six ortho-carbon atoms clearly appeared in the spectrum on both sides of the main band at approximately 30.2 G, 12.7 G, and 10.24 G. In a more detailed picture of the spectrum (Fig. 2c), two pairs of weak and flanking bands appear as shoulders of the main band. These lines can be assigned to those radicals that contain a ¹³C nucleus in *para*-position ($a \sim 3.0$ G) and in *meta* position ($a \sim 1.8$ G), respectively. All these splitting values directly give the isotropic hyperfine interaction between the unpaired electron and the corresponding ¹³C nucleus and they are a measure of the distribution of the spin density in the molecule.

The conformation adopted by this trianion radical in solution has a large effect on the unpaired spin density distribution. This molecule is far from being planar because the phenyl rings are too



Fig. 2. (a) EPR spectrum of TSPTM trianion radical in aqueous solution (10^{-3} M) at room temperature (microwave power, 8 mW; modulation frequency, 100 kHz; modulation amplitude, 0.5 G) and amplification showing ¹³C couplings. (b) Computer simulation with the parameters given in the text.¹⁰ (c) A detailed spectrum showing the overlapped bands corresponding to the coupling with *para*-¹³C atoms (*a* ~ 3.0 G) and *meta*-¹³C atoms (*a* ~ 1.8 G).

bulky and they must twist substantially out of plane, decreasing the conjugation of the π -electron system. Hence the small coupling values with the ¹³C nuclei mainly those in *meta* and *para*-positions. Besides, there was no trace of hyperfine splitting from ³³S of the acid functions, which has a natural abundance of 0.75% and is the only stable sulfur isotope with a nuclear spin *I*=3/2. The twisted conformation shields the central carbon atom bearing the majority of the spin density from the environment and is responsible of the great chemical and thermal stability.

The cyclic voltammetry (CV) methodology as an important tool for understanding the electrochemical behavior of compounds is closely correlated with the scavenging activity for some radical oxygen species. In stable radicals of the PTM series, the electrochemical processes are intimately related with the radical character of the molecule. Values for the electrochemical parameters of the TSPTM radical and for the antioxidants are displayed in Table 1. Cyclic voltammograms showed a quasi-reversible oxidation couple for catechol (Fig. S1), and irreversible oxidation peaks for pyrogallol (Fig. S2) and ascorbic acid (Fig. S3). The cyclic voltammogram of TSPTM trianion radical recorded in water (10^{-3} M) using lithium perchlorate (10^{-1} M) as supporting electrolyte on Pt as electrode, showed a quasi-reversible one-electron reduction (difference between the anodic and cathodic peak potentials, $E_p^a - E_p^c$, of 0.137 V at scan rate $\nu = 200 \text{ mV s}^{-1}$ and 0.88 V at $\nu = 20 \text{ mV s}^{-1}$) with a standard potential $E^0 = -0.42$ V versus SCE, attributed to the addition of one electron to the trivalent carbon atom, $A^{\bullet} \rightarrow \Rightarrow A^{-}$ (Fig. S4). This reduced species is rapidly and quantitatively protonated to the corresponding C–H derivative, α H-TSPTM^{3–}, on the basis of the pK_a value (13.1) reported before. In fact, in the reaction of TSPTM radical

Table 1

CV results for the reduction of the TSPTM radical and the oxidation of polyphenols (1.0 mM of substrate) in 0.1 M LiClO₄ aqueous solution on Pt electrode at 50 mV s⁻¹ and 25.0 °C under Ar atmosphere

Compound	$E_{\rm onset}^c/V$	E_p^c/V	$E_{\rm red}^0/V$	$E_{ m onset}^a/V$	E_p^a/V	$E_{ m ox}^0/V$
TSPTM radical	-0.31	-0.47	-0.42			_
Cathecol	_	—	_	0.18	0.41	0.36
Pyrogallol	_	—	_	0.13	0.48	_
Ascorbic acid	_	_	—	0.01	0.36	_

Potential values versus SCE. E_{conset}^c or E_{onset}^a : initial potential for the cathodic or the anodic peak. E_p^c or E_p^a : Cathodic or anodic peak potential. E_{red}^0 or E_{ox}^2 : standard reduction or oxidation potential for the corresponding couple.

with the antioxidants monitored by UV–vis spectroscopy, the band of the radical diminishes while the typical band of the α H-TSPTM^{3–} increases. The reaction mechanism in the cathode may be described as shown in Scheme 4.



2.2. Radical-scavenging capacity

The TSPTM trianion radical-scavenging capacity of ascorbic acid as a paradigm of antioxidants, and of pyrogallol and catechol, as component moieties of many natural polyphenolic antioxidants, was evaluated by EPR in water. The course of these experimental tests was monitored by recording the decay of the double integral of the band of **1** (g=2.0022) displayed in the spectrum in the presence of the antiradical. The results for pyrogallol are illustrated in Fig. 3,¹¹ where it can be seen the time evolution of the radical concentration and an estimation of the second order rate constant (Results for ascorbic acid and catechol in Figs. S5 and S6). Kinetic parameter values, such as rate constant¹² and stoichiometry¹³ of the reactions are summarized in Table 2. These reactions like those of PTM with ascorbic acid, and HNTTM and TNPTM with polyphenols proceed by electron transfer to TSPTM trianion radical.



Fig. 3. (a) Decay of the intensity (double integral) of the band in the EPR (g=2.0022) of an aqueous solution of TSPTM trianion radical/pyrogallol (molar ratio: 10:1). (b) Estimation of the second order rate constant k=1.5 M⁻¹ s⁻¹¹¹ for the first hour of the reaction between TSPTM trianion radical and pyrogallol (molar ratio, 10:1).

Table 2

Observed rate constants (k) and stoichiometric values (n) for the reaction of TSPTM trianion radical with ascorbic acid, pyrogallol, and catechol in aqueous solution

Compound	$k (\mathrm{M}^{-1}\mathrm{s}^{-1})$	n
Ascorbic acid	33	3.5
Pyrogallol	1.5	6-7
Catechol	0.05	_

Now the generated tetraanion TSPTM^{4–} is rapidly and quantitatively protonated by water to αH -TSPTM trianion due to the acid character of the aqueous solutions and, therefore, the tetraanion is not observed in UV–vis spectroscopy unlike what it happens with PTM in THF, and HNTTM and TNPTM in non-aqueous solvents.

While ascorbic acid presents a rapid TSPTM trianion radicalscavenging reaction and pyrogallol exhibits a significantly moderate reaction, the reaction of catechol is noticeably slow. The order of activity of the antioxidants is ascorbic acid>pyrogallol>catechol, which is well correlated with their onset anodic peak potentials (Table 1). This selectivity in the activity of the TSPTM trianion radical with ascorbic acid, pyrogallol, and catechol in aqueous medium is also a consequence of its moderate oxidant power and, therefore of its reduction potential. As strong acids, the functional hydroxysulfonyl groups in the TSPTM radical are completely disassociated in water, and the presence of net negative charges $-SO_{3-}$ decreases significantly the electron-withdrawing properties of these substituents, thereby decreasing the oxidant power of the trivalent carbon atom. It is also valuable to mention the high stoichiometric values obtained in the reactions of TSPTM trianion radical with ascorbic acid (3:1, radical/acid) and mainly with pyrogallol (6 or 7:1, radical/pyrogallol) (Table 2). It is known that ascorbic acid scavenges 2 equiv of perchlorotriphenylmethyl (PTM) radical in THF and pyrogallol scavenges 3 equiv of either HNTTM or TNPTM radicals in CHCl₃/MeOH (2:1), roughly one electron per reactive hydroxyl. Table 2 shows that ascorbic acid reduces 3 equiv of TSPTM trianion radical and pyrogallol 6 or 7 equiv of TSPTM radical. All these results indicate that the stoichiometry of these electron transfer reactions largely depend on the applied solvent.

3. Conclusion

In conclusion, this manuscript reports the synthesis of a stable radical of the PTM series very soluble in water. Due to the presence of sulfonic groups in the molecule, aqueous solutions of radical **1** are strongly acidic. It has been characterized by UV–vis and EPR spectroscopy in aqueous solution. It is electrochemically reduced in a quasi-reversible one-electron process to a tetraanion, a charged species very stable in degassed basic aqueous solution, and characterized by UV–vis spectroscopy. TSPTM trianion radical has the ability to react in water with ascorbic acid and pyrogallol by electron transfer processes and it reacts scarcely with catechol. Now we have focused our attention to test the chemosensor properties of TSPTM radical **1** is able to discriminate catechol or pyrogallol moieties from those antioxidants.

4. Experimental

4.1. General procedures

IR spectra were recorded with a FT-IR spectrophotometer, ¹H and ¹³C NMR spectra were collected on a 400 MHz spectrometer at room temperature, electronic spectra with a single cell UV–vis spectrophotometer and the EPR spectra with an EMX-Plus 10/12 spectrometer. Electrospray mass spectra (ESIMS) were recorded on a LC/MSD-TOF.

4.2. Buffer solutions

(a) $pH=12.67\pm0.01$: to an aqueous solution of KCl (0.2 m) (50 mL) was added another solution of NaOH (0.2 M) (12 mL). (b) $pH=12.98\pm0.01$: to an aqueous solution of KCl (0.2 M) (50 mL) was added another solution of NaOH (0.2 M) (132 mL).

4.3. Cyclic voltammetries

Cyclic voltammetries were carried out in a standard thermostated three-electrode cell. A platinum (Pt) disk with 0.093 cm² area was used as the working electrode and a Pt wire as the counter electrode. The reference electrode was a saturated calomel electrode (SCE), submerged in a salt bridge of the same electrolyte, which was separated from the test solution by a Vycor membrane. Solution of TSPTM (**1**) radical ($\sim 10^{-3}$ M) in water containing lithium perchlorate (0.1 M) as background electrolyte was studied. The volume of all test solutions was 50 mL. Electrochemical measurements were performed under an Argon atmosphere (25 °C) using an Eco Chemie Autolab PGSTAT100 potentiostat–galvanostat controlled by a computer with a Nova 1.5 software. Cyclic voltammograms were recorded at scan rates ranging from 20 to 200 mV s⁻¹.

4.4. Kinetic measurements

The kinetic parameters were obtained by EPR. Freshly prepared solutions of TSPTM (**1**) (245 μ M) and ascorbic acid (49 μ M) in degassed water were mixed (1:1, v/v), and TSPTM (**1**) (223 μ M) and catechol (45 μ M) in degassed water were mixed (1:1, v/v) in the spectrometer cell (molar ratios between TSPTM and antioxidant, ~5:1) The EPR spectra were recorded at different intervals.

4.5. Synthesis of tris(2,3,5,6-tetrachlorophenyl-4hydroxysulfonyl)methane (α*H*-TSPTM)

A mixture of tris(2,3,5,6-tetrachlorophenyl)methane (2.0 g; 3.04 mmol) and fuming H₂SO₄ (SO₃, 65%) (60 mL) was stirred (95–110 °C, 5 days). The solution was then poured into cracked ice (200 mL) and kept overnight. The precipitate was separated by filtration, dried (100 °C), and chromatographed by column on silicagel eluting with ethyl acetate/MeOH (5:3, v/v) afforded α H-TSPTM (2.4 g; 89 %) as a white ugly solid: UV–vis (H₂O) λ_{max} /nm (ε ;/Lmol⁻¹ cm⁻¹) 304 (3640), 312 (4305); IR (KBr, cm⁻¹): 3439 (OH), 2800–2900 (C–H, alf-H), 1651 (aromatic ring), 1311, 1289, 1203, 1118, 1055, 807, 786, 731, 699, 612, 509; ¹H NMR (D₂O, 300 MHz): δ 7.130 (s, 1H, α -H); ¹³C NMR (D₂O, 500 MHz) δ 141.4, 140.0, 137.2, 136.4, 133.3, 132.2, 30.8; ES-HRMS (–) calcd for [C₁₉HCl₁₂O₉S₃]² 447.7524, found *m*/2 447.7563; calcd for [C₁₉H₂Cl₁₂O₆S₂]² 407.2701, found *m*/2 407.2717; calcd for [C₁₉HCl₁₁O₆S₂]² 388.7871, found *m*/2 388.7886; calcd for [C₁₉Cl₁₂O₉S₃]³ 298.1673.

4.6. Synthesis of tris(2,3,5,6-tetrachlorophenyl-4hydroxysulfonyl)methyl (TSPTM) radical

To a stirred solution of α *H*-TSPTM (508 mg; 0.64 mmol) in THF/ H₂O (5:1) (60 mL) at room temperature, an aqueous solution of KOH (1 M) (2.5 mL) was added and the strong red solution was stirred overnight. Chloranil (0.528 g; 2.1 mmol) was added in one portion and the solution was stirred further (6 h). Afterward, the solution was evaporated at reduced pressure and the residue was digested in ethyl acetate/methanol (2:1). The insoluble fraction, separated by filtration and dried, gave a pale red solid (592 mg), which was dissolved in MeOH and treated with Amberlite IRA-120 (1.48 g). The mixture was stirred at room temperature (12 h). The Amberlite was separated by filtration and the solution was dried to give TSPTM radical (496 mg; 98%) as a solid dark red: UV–vis (H₂O) $\lambda_{max}/nm (\epsilon/Lmol^{-1} cm^{-1}) 301 (5905)$, 368 (sh) (8970), 385 (17,500), 504 (745), 556 (615). IR (KBr, cm⁻¹) 3427 (vs), 1308 (s), 1211 (s), 1117 (m), 1065 (s), 788 (m), 613 (s). ES-HRMS (–) calcd for $[C_{19}HCl_{12}O_9S_3Na]^{2-}$ 458.7434; found *m*/2 458.7414; calcd for $[C_{19}HCl_{12}O_9S_3]^{2-}$ 447.7524, found *m*/2 447.7524; calcd for $[C_{19}HCl_{11}O_6S_2]^{2-}$ 388.7877; calcd for $[C_{19}Cl_{12}O_9S_3]^{3-}$ 298,1658, found *m*/3 298.1659.

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Supplementary data

Cyclic voltammograms of radical **1** ascorbic acid, pyrogallol, and catechol, ¹H and ¹³C NMR spectra of α *H*-TSPTM, and graphics for kinetic results of radical **1** with ascorbic acid and catechol. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.02.069.

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- 7. The pK_{HA} of α H-TSPTM in water was calculated from two buffer solutions at pH 12.67±0.01 and 12.98±0.01, and the absorptivity of the colored anion in the UV–vis spectrum.
- 8. This is a general adopted conformation for the radicals of PTM and TTM series conferring a great stability to these radical species.
- An example of the stability of radical 1 is that it is practically quantitatively recovered from degassed aqueous solutions after two days in the dark.
- The spectrum was simulated following the WINSIM program provided by Dulog, D. Public EPR Software Tools; National Institute of Environmental Health Sciences: Bethesda, MD, 1996.
- 11. Freshly prepared solutions of TSPTM trianion radical in water (490.6 μ M) and the pyrogallol (47.6 μ M) in water were mixed (1:1, v/v) in the spectrometer cell of the EPR (molar ratios between trianion radical and pyrogallol, ~10:1).
- 12. Values of the kinetic rate constants of the reactions of TSPTM trianion radical with the reported antioxidants have been carried out following the general kinetic model reported by Dangles et al. Goupy, P.; Dufour, C.; Loonis, M.; Dangles, O. J. Agric. Food Chem. **2003**, *51*, 615–622.
- 13. The *n* values of the stoichiometry of the reactions were calculated using the equation: $n = c_0^{\text{rad}}[(1 A_f/A_0)]c_0^{\text{antiox}}$, where A_0 and A_f are the initial and final double integral of the EPR band, respectively, c_0^{rad} is the initial concentration of the radical and c_0^{antiox} is the initial concentration of the antioxidant.