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Deposition Efficacy of Natural and Synthetic Antioxidants on Fabrics

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Abstract: Pine bark extracts were tested as valid natural alternatives to common phenolic antioxidants to be deposited onto solid matrices. An analytical method for determining both deposition-efficacy and maintenance of antioxidant activity on fabrics surfaces was developed and successfully applied to phenolic antioxidants and pine tannins onto cotton fabric samples. Accumulated data suggest that common phenolic antioxidants and tannin contribute to an elevated antioxidant activity on fabric. A known source of odour is autoxidation of residual sebum on fabric, leading to the generation of malodourous compounds. Therefore, antioxidants hold the promise for mitigating malodour on fabrics, a top unmet consumer need around the globe.

Keywords: antioxidants; tannin; pine bark extract; fabric antioxidant activity; ABTS; malodour

1. Introduction

Tannins are structurally different polyphenolic secondary metabolites of plants. Besides their polyphenolic character, they offer a wide range of interesting biological functional features, besides biocompatibility and biodegradability, namely antioxidant, antimicrobial and anti-inflammatory activities [1–9], that render them ideal for several applications such as topical cosmetics, and biomedical and healthcare products.

Tannins have been used in textiles for several hundreds of years and nowadays their use as natural dyes in textile applications is rapidly growing because of the potential carcinogenicity and environmental effects of synthetic dyes [10–13]. Moreover, tannin-rich natural extracts were used as a colouring as well as antimicrobial agents to treat cotton fabrics [14,15]. Hence, on one side, natural extracts can be successfully used as natural dyes, and on the other side, they also impart an antimicrobial finish to cotton fabric, representing viable alternatives to the artificial and sometimes toxic antimicrobial agents for hospital textiles as well as agents to hinder malodorous species which may be formed by the enzymatic oxidation of fatty acids present in domestic laundry soils. The malodour draws its origin from the bacterial biotransformation of proteinaceous substrates and odourless physiological secretions containing long-chain fatty acids, sulphur-containing amino acids and hormones, into volatile odorous

organic compounds [16,17]. Body soils left behind on fabrics will break down over time due to microbial action or autoxidation into malodorous byproducts which consumers describe as body, sweat, stale, or musty odours [18–21]. The process can be suppressed by antioxidant agents that are able to interfere with the oxidation of organic body soil caused by microorganisms belonging to skin flora, thereby limiting the formation of malodour. In the US, 45.7% of consumers claim "odour removal" as a need in at least one out of their last ten loads (Procter and Gamble, unpublished data from a 2019 study involving 4995 representative US consumers). Odour removal is also a top unmet need in many other regions. Thus, more effective laundry detergent solutions are needed to eliminate odours from fabrics. Given that tannins possess significant antioxidant and enzyme complexing properties associated with a high propensity to form complexes, they can significantly contribute to malodour reduction. Furthermore, tannins deposited on fabrics can undergo stacking and thus trap the malodorous species on fabrics. Several studies aiming at evaluating the possible effects of polyphenolics from plant extract on malodour have demonstrated their effective role as malodour-reducing agents [22–27].

Existing literature suggests that condensed tannins are able to deposit on fabrics [28–30]. Their specific UV absorbance characteristics can also make tannins natural sunscreens [31,32]. These specific characteristics make tannins an interesting starting point for the development of smart textiles, which, owing to their added properties, show sunscreen, antimicrobial and malodour control properties and enable prevention of malodour formation also in a re-blooming scenario.

In this context, in a preliminary study aimed to assess the possibility of using pine bark extracts as natural active ingredients in smart textiles [21–27], we deposited on cotton samples two different pine tannins as well as common phenolic antioxidants, namely 3,5-di-*tert*-butyl-4-hydroxy toluene (BHT), methyl 3-(3,5-di-*tert*-butyl- 4-hydroxyphenyl)propanoate) (M*t*BHPP) and octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoate (Figure S1 in Supplementary Materials).

A fast analytical method based on the 2,2′-azino-bis (3- ethylbenzothiazoline-6-sulfonic acid) radical cation ($ABTS^{\bullet+}$) decolourisation assay [33] was used and adapted to meet the needs emerging from the double objective of determining antioxidant activity of tannins and phenolic antioxidant-treated fabrics, as well as to quantitatively determine the concentration of active antioxidants deposited on the fabric samples based on specific calibrations accounting for specific antioxidant species.

2. Materials and Methods

2.1. General

Industrially tannin-pretreated fabrics were obtained from Procter and Gamble Company (Cincinnati, OH, USA). Bark chips from *Pinus sylvestris* and *Pinus taeda* were extracted in water spiked with sodium salts, or with an aqueous solution of acetone; the pine tannins obtained are namely water-extracted *Pinus sylvestris* tannin (**PST-sW1**) and acetone/water-derived *Pinus taeda* tannin (**PTT-AW1**).

Furthermore, 2,2′-azino-bis (3- ethylbenzothiazoline-6-sulfonic acid) (ABTS) diammonium salt, sodium persulfate, ascorbic acid and butylated hydroxytoluene (BHT) were purchased from Sigma Aldrich, octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propanoate from BASF (Ludwigshafen, Germany) and methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propanoate (M*t*BHPP) from Milliken (Spartanburg, SC, USA). Heavy duty laundry detergent Ariel (HDL) was manufactured by the Procter and Gamble Company (Cincinnati, OH, USA).

2.2. Pine Tannin Isolation

In order to produce **PST-sW1** sample, small wood grains were subjected to a first extraction by stirring in water spiked with sodium bisulphite (2% $NaHSO_3$) for two hours at 80 °C in a 10:1 (w/w) liquor-solid ratio; after a filtration step, a second extraction was performed by stirring in water spiked with sodium bisulphite (2% $NaHSO_3$) for two hours at 80 °C in a 5:1 (w:w) liquor-solid ratio; finally,

the solid residue was filtered off and the extractive was finally concentrated under reduced pressure at the rotary evaporator. Typically, a 500 g batch of bark yielded around 40-50 g solid extracts.

In order to produce the **PTT-AW1** sample, small wood grains of pine bark were suspended in a 70/30 (v/v) acetone/water mixture in a 10:1 (w:w) liquor-solid ratio and kept under reflux for 8 h. The solid residue was separated from the liquor by centrifugation and washed with the same solvent mixture. The extractive was finally concentrated under reduced pressure at the rotary evaporator. Typically, a 500 g batch of bark yielded around 30–35 g solid extracts.

2.3. Fabric Sample Treatments

Industrial treatment: In order to obtain a forced deposition of antioxidants onto textiles, fabric samples were brought in contact with an aqueous solution (80 ppm) in water or HDL (Heavy Duty Laundry detergent). Two protocols where used to perform forced deposition treatments by means of a mechanical stirrer (phenolic antioxidants) or using a launderometer (tannins).

Launderometer procedure: Tannin powder was pre-dissolved in monopropylene glycol at a concentration of 5% (w/w). Then the tannin solution was added at a concentration of 80 ppm tannin to either (i) 200 mL tab water or (ii) 200 mL tab water containing 1.03 g liquid detergent solution.

For each test, the launderometer jar was loaded with two pieces of fabric, sized 5 cm × 5 cm per piece of fabric: one piece of fabric of knitted cotton, and one piece of fabric polyester. A total of 200 mL of the tannin/water or tannin/water/liquid detergent solution is added in the launderometer jar containing the fabrics. Five metal spheres are added to each jar for agitation. The launderometer cycle time was set to 2 h, temperature was set to 30 °C. After the launderometer cycle, the fabrics were gently squeezed and rinsed with tab water for 5 min. Fabrics were squeezed again and air dried.

Laboratory treatment: In order to obtain a forced deposition of antioxidants onto textiles, a piece of cotton fabric sample (10 mg, 0.25 cm^2) was transferred into a falcon tube containing 10 mL of the selected aqueous antioxidant solution (0.1 mg/mL). The mixture was vortexed for two minutes to facilitate the deposition on the fabric matter. The fabric sample was removed from the falcon tube, washed by vortexing in 10 mL of distilled water for two minutes and air-dried.

2.4. Antioxidant Activity Test

Antioxidants in aqueous solution*:* Antioxidant activity in solution was measured using the ABTS radical cation ($ABTS^{\bullet+}$) decolourisation assay with some modifications [33,34]. Radical scavenging capability of the tannin in aqueous solution was determined by measuring the decrease in absorbance of $ABTS^{\bullet+}$ at λ = 730 nm after a fixed incubation time of the radical cation solution with the sample to be tested using a spectrophotometer with a thermostatic cell container equilibrated at 30 °C. $ABTS^{\bullet+}$ was produced by reacting ABTS (7.00 mM final concentration) with sodium persulfate (2.45 mM final concentration); the mixture was allowed to stand in the dark at room temperature for 12–16 h before use (oxidation of the ABTS starts immediately, but the absorbance was not found stable before 6 h of reaction time). The radical is stable in this form for two days when stored in the dark at room temperature. Aqueous $ABTS^{\bullet+}$ solution (7.00 mM) was diluted with distilled water to an absorbance in the range of 0.65–0.70 and equilibrated at 30 °C. After addition of 1000 µL of this diluted $ABTS^{\bullet+}$ solution to 10 µL of aqueous tannin solution (1 mg/mL) or alternatively 10 µL of a phenolic antioxidant compound (final concentration range 0–25 mM), the absorbance reading was taken exactly at 30 °C, 1 min after initial mixing. An appropriate blank was run in the assay. The percentage inhibition of absorbance at λ = 730 nm was calculated and plotted as a function of concentration of antioxidant related to the standard reference data, i.e., mg of ascorbic acid equivalent (AAE) per mg of dry antioxidant substance.

Actives deposited on fabric*:* Antioxidant activity of actives deposited on fabric was measured using an adopted $ABTS^{\bullet+}$ decolourisation assay. After addition of 1.0 mL of diluted $ABTS^{\bullet+}$ solution ($A_{730nm} \approx 0.7$; see above) to 10 mg treated fabric sample, or, alternatively, 10 µL of phenolic antioxidant compounds or antioxidant standard (final concentration range 0–25 µm) the absorbance reading was

taken exactly 1 min after initial mixing at 30 °C after an ultimate shake of the solution approximately 5 s before measurement, to allow the paper to sink to the bottom prior to the measurement. A blank was run in the assay using a nontreated fabric sample. The percentage inhibition of absorbance at λ = 730 nm was calculated and plotted as a function of concentration of actives related to the standard reference data, i.e., as µg of ascorbic acid equivalent (AAE) per 10 mg fabric portion.

Amount of antioxidant industrially deposited on fabric: The amount of deposited antioxidant was determined by measuring the absorbance decrease, after a fixed incubation time, of $ABTS^{\bullet+}$ solution ($A_{730nm} \approx 0.7$; see above) with treated fabric samples (weighing 10.0 mg each), based on a specific calibration curve (final concentration range 0–2.5 µg/mL) obtained with the same approach and using an aqueous antioxidant solution accounting for the antioxidant type used.

2.5. Tannin Characterisation

^{31}P NMR: ^{31}P NMR analysis was performed after the derivatisation of accurately weighed tannin samples (10–15 mg) with the reagent 2-chloro-4,4′,5,5′-tetramethyl-1,3,2-dioxaphospholane, against cholesterol as internal standard according to methods previously published [35–38], using an inverse-gated pulse-sequence on either a Bruker, Billerica, MA, USA, 300 MHz or a Bruker 700 MHz NMR spectrometer, controlled via TopSpin software packages.

Gel permeation chromatography *(GPC)*: Approximately 3.0 mg of tannin was suspended in 1.0 mL of glacial acetic acid/acetyl bromide (9:1 (v/v)) for 2 h in accordance with the method provided for lignins by Asikkala et al. [39]. The solvent was then removed under reduced pressure, and the residue was dissolved in HPLC-grade THF and filtered over a 0.45 µm syringe filter prior to injection. GPC analyses were performed as described before [40] using a Shimadzu, Kyoto, Japan, instrument, consisting of a controller unit (CBM-20A), a pumping unit (LC 20AT) equipped with a 20 µL sample loop, a degasser unit (DGU-20A3), a column oven (CTO-20AC), a diode array detector (SPD-M20A), and a refractive index detector (RID-10A); the Shimadzu LabSolution software package (Version 5.42 SP3) was used for system control. Three analytical GPC columns (each 7.5 × 30 mm) were connected in series for the analyses—an Agilent Technologies, Santa Clara, California, USA, PLgel 5 µm 10 000 Å, followed by an Agilent PLgel 5 µm 1000 Å and an Agilent PLgel 5 µm 500 Å. Calibration was performed with polystyrene standards (Sigma Aldrich/Merck KGaA, Darmstadt, Germany, MW range: 162–5 × 10^6 g/mol). Final analyses of each sample were performed as described elsewhere [40].

Folin–Ciocalteau test: The total phenolic content of the extracts was determined by the Folin–Ciocalteu method: 2.5 mL of Folin-reagent (diluted 10 times) was added to 0.5 mL of a solution of tannin in distilled water (0.10 mg/mL). After 2 min, 2.0 mL of sodium carbonate (7.5% (m/m)) was added. The mixture was heated at 50 °C for 5 min. Absorbance was read at λ = 765 nm in suitable cuvettes. A calibration curve was obtained following this approach using a solution of gallic acid in distilled water (0.5 mg/mL). Results are reported as mg of gallic acid equivalent (GAE) per mg of dry tannin (mg GAE/mg tannin) [41]. Measurements were done using a Shimadzu, Kyoto, Japan, 1800 UV spectrophotometer.

Scalbert test: The proanthocyanidin content of pine tannins was determined by the Scalbert method [42]. A total of 5.0 mL of an acidic ferrous solution (77 mg $FeSO_4 \cdot 7\ H_2O$ in 500 mL HCl/BuOH (2/3)) was added to 0.5 mL of the aqueous tannin solution (1 mg/mL). Mixtures were heated at 95 °C for 15 min. Absorbance was read at λ = 530 nm. Results are expressed in cyanidin equivalents (CyaE) as mg per g of dry bark (mg CyaE/g bark). Measurements were done using a Shimadzu, Kyoto, Japan, 1800 UV spectrophotometer.

3. Results and Discussion

3.1. Pine Tannin Isolation

In order to develop a general protocol for the characterisation of antioxidant activity of tannins on fabric surfaces and to determine the amounts of deposited tannin on the fabrics, we selected two different

extraction protocols in water spiked with sodium salts and aqueous solution of acetone, respectively. It has been reported in literature that extraction of pine bark using water spiked with sodium bisulphate or sodium carbonate and water mixed with acetone yields tannin extracts with different compositions and characteristics [42–45]. More specifically, the extraction with aqueous acetone is supposed to result in a preferential isolation of high-molecular-weight polyphenols, while oligomers with lower degrees of polymerisation are isolated upon extraction with aqueous salt solutions.

These two different types of pine tannins (**PT**), termed **PST-sW1** and **PTT-AW1**, respectively, were obtained in 30% and 6% yield of dry tannin mass, respectively. **PST-sW1** was found to contain 52% (m/m) residual sulphites.

3.2. Structural Aspects of Pine Tannin

The structural characterisation of the tannins consisted of the determination of the distribution of molecular weights by means of gel permeation chromatography (GPC), the total phenol content by spectrophotometry using the Folin–Ciocalteau test [41], ^{31}P NMR analysis of the different phenolic groups and the proanthocyanidin content of pine tannins using the Scalbert method [42].

In view of the fact that selected properties, i.e., antioxidant activities, of natural resources that render them potential natural active ingredients to be used in the target products are significantly correlated with their prevailing structural features [46–54], polyphenolic and proanthocyanidins features of pine tannins are crucial aspects to know for an overall data interpretation. Selected structural data related to the characterisation of different pine bark extracts are summarised in Tables 1 and 2.

Table 1. Structural characteristics obtained for pine tannins (**PT**).

Entry	Pine Tannin	Extraction	M_n [Da] [a]	Total Phenolic Content [mg GAE/mg PT] [b]	Proanthocyanidin Content [mg CyE/g] [c]
1	**PST-sW1**	water/2%$NaHSO_3$	500	0.15	22
2	**PTT-AW1**	acetone/water	530	0.23	43

[a] Determined by GPC in THF after acetobromination of the sample; results reflect the soluble part. Numbers in square brackets represent exact molecular weight; [b] Determined by Folin–Ciocalteau test; [c] Determined by Scalbert test.

Table 2. Averaged quantitative structural characteristics obtained for pine bark extracts of by quantitative ^{31}P NMR.

OH-Group/Motif	Integration Range [ppm]	Av. Abundance [mmol g^{-1}]	
		PTT-sW1 [a]	PTT-AW1
aliphatic	145.94–145.25	3.11 ± 0.5	2.22 ± 0.2
ortho-disubstututed OH	142.46–141.06	0.56 ± 0.5	0.77 ± 0.2
gallo/epigallocatechin	142.46–141.87	1.22 ± 0.5	0.39 ± 0.2
gallate	141.47–141.05	0.01 ± 0.5	0.12 ± 0.2
ortho-substituted OH	140.60–137.60	1.00 ± 0.5	1.66 ± 0.2
catechol	140.20–138.30	0.89 ± 0.5	0.72 ± 0.2
non-catechols	138.80–137.60	0.44 ± 0.5	0.91 ± 0.2
ortho-unsubstituted OH	137.60–137.40	0.11 ± 0.5	0.79 ± 0.2
acidic	135.50–134.00	0.44 ± 0.5	0.82 ± 0.2

[a] Sample only scarcely soluble under standardised analysis conditions, approx. 10–15% of the sample was adequately solubilised.

Tannins arising from extraction using both aqueous acetone and sulphite-containing water exhibit mean average molecular weights (Mn) of around 500 Da. The results indicated that both extraction methods are suitable for extracting tannins with comparable molecular weight from the bark matrix but with different content of phenols and condensed tannins, higher in the case of **PTT-AW1** (Table 1, entry 2).

The ^{31}P NMR spectra (Figure 1A and data (Table 2)) reveal that pine tannins are essentially comprised of catechin/epicatechin units, with some gallocatechin/epigallocatechin moieties as well as gallates incorporated. Figure 1B shows a representative structure of the main composition, in which the GPC-derived data regarding the number average molecular weight (Mn) were used for estimating an average degree of polymerisation (DP) equal to three.

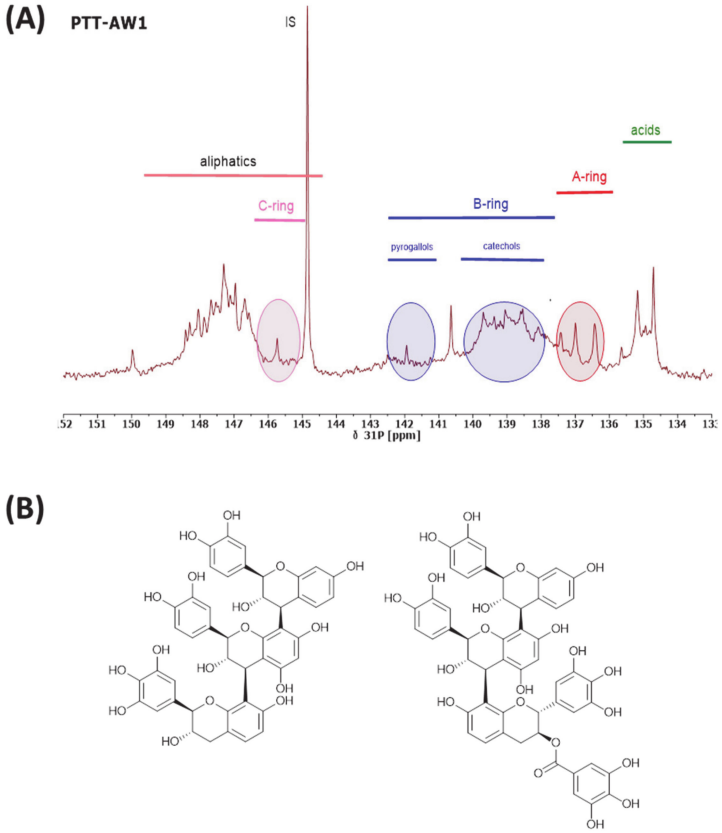

Figure 1. (**A**) Representative ^{31}P NMR of a **PTT-AW1** with cholesterol as internal standard (IS); (**B**) structural representations of pine tannin (**PT**), estimating trimeric 4α–8 linkage.

Various extraction methods yield tannins with different degrees of carbohydrate contaminations, as delineable from the structure that the overestimated aliphatic OH-group content shows. While aqueous acetone extractions furnish tannins with a relatively low carbohydrate content, sulphite-assisted aqueous extractions cause more significant co-extraction of carbohydrates. A difficulty in the preparation of **PST-sW1** was identified in the efficient removal of all inorganic salts, which requires eventually an additional washing of the extracts prior to drying; generally, **PST-sW1** preparations exhibit scarcer solubilities (*vide infra*, Figure 2). As can be expected, despite overall structural similarity, differences in the absolute distribution of typical pine tannin motifs are noticeable in the ^{31}P NMR. A more detailed discussion of this aspect is, however, not possible given the solubility characteristics of the tested **PST-sW1** preparation.

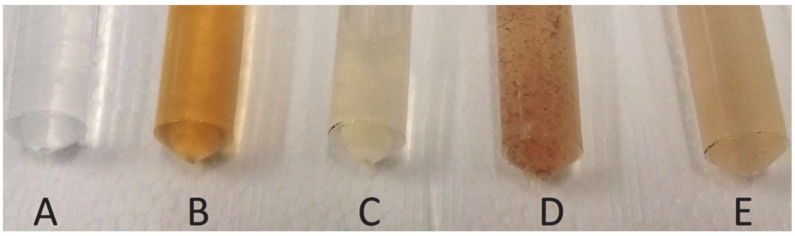

Figure 2. Representative starting tannin solutions used in the ABTS$^{\bullet+}$ decolourisation assay; aqueous ethanol (70%) sample solutions (**A**,**B**,**E**) and aqueous sample solution (**C**,**D**).

Further analytical data were not generated for the different tannin extracts, since this work was more intended as an exploratory study regarding the application of the prepared pine bark tannins.

3.3. Antioxidant Activity Test in Solution

Several available methods to test the antioxidant activity of different compounds are reported in the literature [33,34,53,55–58]. Among them, those based on direct measurement of radical scavenging capability are the most widely used ones. They are less expensive and less time-consuming in comparison to the inhibition procedures in which the inhibition of oxidative damage of a target molecule is measured in the presence of the examined antioxidants [59,60]. Based on what was found in the literature, the currently most common methods for analysing the antioxidant capability of compounds deposited on fabrics use chromogen compounds of a radical nature are the stable free radicals 2,2-diphenyl-1-picrylhydrazyl (DPPH$^{\bullet}$) and 2,2′-azino-bis (3-ethylbenzothiazoline-6-sulphonic acid) (ABTS$^{\bullet+}$) [61–66]. Both display a remarkable stability in specific assay conditions but also present several differences in their response to the antioxidants [67,68]. DPPH is a stable and commercially available organic free radical with a peak of absorbance at λ = 515 nm. It undergoes a decrease in its absorption when reduced by an antioxidant or a free radical species. While ABTS$^{\bullet+}$ can be solubilised in aqueous and organic solvents, in which the antioxidant activity can be measured due to the hydrophilic and lipophilic nature of the compounds in samples, on the contrary, DPPH cannot be dissolved in aqueous solvents but only in organic ones, which is an important limitation when interpreting the role of hydrophilic antioxidants. Moreover, as it is reported in literature [68], a possible colour interference of DPPH with the plant material extracts can lead to underestimation of antioxidant activity. Therefore, in order to minimise a potential interference with the pine tannins being studied and thus with the aim to obtain more reliable data, the antioxidant activities of cotton fabrics were investigated using the quick and easy colorimetric procedure based on the ABTS assay, also characterised by measurement simplicity and short experimental time.

Preliminarily, we determined the antioxidant activity of two different pine tannins and of BHT, M*t*BHPP and octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propanoate in solution by carrying out the ABTS$^{\bullet+}$ decolourisation assay; results are reported in Table 3. Due to the solubility issues in water observed for **PTT-AW1** (Figure 2D), the antioxidant activity measurements were repeated using aqueous ethanol (30% (v/v) water) as a solvent for preparing the starting antioxidant solution (Figure 2B). **PST-sW1** as water soluble extract (Figure 2C) gave reliable data in the standard ABTS assay run with water as only solvent. Since **PST-sW1** was equally soluble in the aqueous ethanol necessary for solubilising **PTT-AW1**, it was used for creating data for comparison for estimating the differences in observed antioxidant activity as a function of the test used.

Table 3. Antioxidant capabilities of pine tannins and commercial synthetic antioxidant as reference.

Entry	Pine Tannin	Extraction	Anti-Ox Activity [mg AAE per Mg Pine Tannin] [a]
1	**PST-sW1**	water/2%$NaHSO_3$	0.30, 0.40 [b], 0.40 [c]
2	**PTT-AW1**	acetone/water	0.05, 0.11 [b], 0.05 [d]
3	BHT	—	0.14 [b]
4	octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	—	0.03 [b]
5	M*t*BHPP	—	0.01 [b]

[a] Determined by a standard ABTS-assay if not stated otherwise. The maximum semi-dispersion is adopted for the error estimation (±0.01).[b] Determined by a slightly modified ABTS-assay, using a starting aqueous ethanol (70%) sample solution to be run in the assay instead of the aqueous one. [c] Determined by running in the modified ABTS-assay (started from an aqueous ethanol (70%) pine tannin) only the supernatants obtained after centrifugation at 5000 rpm for 1 min of the pine tannin starting liquid suspensions. [d] Determined by running in the standard ABTS-assay only the supernatants obtained after centrifugation at 5000 rpm for 1 min of the pine tannin starting liquid suspensions.

Overall, a slightly better antioxidant activity was observed in the case of the use of starting pine tannin preparations in aqueous ethanol instead of water (Table 3, entries 1 and 2) a fact that could be ascribed to an increased solubility in this solvent system of those components responsible for the radical scavenging capability. Therefore, the use of aqueous ethanol for both the samples allowed bringing in solution a greater quantity of components responsible for the antioxidant activity. Noteworthy, after centrifugation of the starting liquid suspensions of tannins (Figure 2D,E) and performing the measurements only with the supernatants, respective AAE values essentially did not change (Table 3, entries 1 and 2). This evidence suggests that the insoluble part does not significantly contribute to the antioxidant activity of the sample.

In conclusion, **PST-sW1** shows a better radical scavenging activity (Table 3, entry 1) but a lower content of phenols and condensed tannins in comparison to **PTT-AW1**, despite having similar molecular weight (Table 1).

Since the antioxidant activity of the plant extracts is mainly attributed to the high levels of phenolics and proanthocyanidins [51,69], these findings suggest that some other constituents, impurities or a combination of them, due to the extraction procedure, might be co-responsible for the actual radical scavenging activity.

In Table 3, entry 3, we report the AAE values of synthetic antioxidants BHT, M*t*BHPP and octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoate, as references (Figures S1 and S2 in Supplementary Materials), as common food additives and ingredients in personal care cosmetics, pesticides and other consumer products [70,71]; their antioxidant activity exhibited in the $ABTS^{\bullet+}$ assay is comparable to that one observed for **PTT-AW1**, the pine tannin sample with a lower activity (Table 3, entry 2). This evidence hence lends pine tannins to be a natural viable alternative to the artificial antioxidant agents used in many industrial application and formulations.

3.4. Antioxidant Activity on Fabrics

In order to obtain smart textiles, we subsequently deposited the two pine tannins and the commercial antioxidants previously selected onto cotton fabric samples and investigated their maintenance of functional features, especially the antioxidant activity. For this purpose, each treated fabric was subjected an adapted $ABTS^{\bullet+}$ decolourisation assay. Results are summarised in Table 4. Antioxidant activities of cotton fabrics significantly increased after the antioxidant deposition treatments, and the lowest ant-oxidative capacity is shown for the reference fabric. This could be attributed to the retention of antioxidants on the treated fabric surface.

Table 4. Antioxidant activity data obtained for cotton fabric samples treated with pine tannins.

Entry	Fabric Sample [10 mg]	Treatment Conditions	Anti-ox Activity [μg AAE per Fabric Portion] [a]
1	**PST-sW1**_cotton	H_2O_mechanical	0.37 ± 0.22
2	**PST-sW1**_cotton	HDL mechanical	0.16 ± 0.11
3	**PTT-AW1**_cotton	H_2O_mechanical	0.48 ± 0.22
4	**PTT-AW1**_cotton	HDL mechanical	0.41 ± 0.23
5	**PST-sW1**_cotton	H_2O	0.42 ± 0.11
6	BHT_cotton	H_2O_mechanical	0.18± 0.22
7	BHT_cotton	H_2O_	0.20± 0.22
8	M*t*BHPP_cotton	H_2O_mechanical	0.24± 0.22
9	M*t*BHPP_cotton	H_2O_	0.27± 0.22
10	cotton	H_2O mechanical	0.00 ± 0.10
11	cotton	HDL_mechanical	0.00 ± 0.10
12	cotton	H_2O	0.00 ± 0.10

[a] The maximum semi-dispersion is adopted for the error estimation. More in detail, as can be seen in Table 2, entries 1 and 5, the values obtained for the measurements show that there is not a substantial difference between fabrics treated industrially or in the laboratory. Noteworthy, combined data analysis shows a larger relative variance for mechanically treated samples. This fact could be explained by a non-homogenous tannin deposition especially in case of mechanical treatment (see below).

The data reveal that treated fabric samples, i.e., industrial treatment (Table 4, entries 1–4) and laboratory treatment, (Table 4, entry 5) in comparison to control-fabrics (Table 4, entries 6–8), display an antioxidant activity under all treatment conditions. Most importantly, this observed activity for all treated fabric samples is comparable in all cases except for **PST-sW1** industrially treated in the presence of HDL (Table 4, entry 2): this sample exhibits lower antioxidant activity.

3.5. Determination of Antioxidant Concentration Deposited on Fabric

The assessment of the amount of antioxidant deposited on fabrics is of crucial relevance in view of many possible practical applications. In this effort, a protocol for the quantification of single antioxidant deposited was developed. Samples of fabrics (weighing 10.0 mg each), were used assuming the following: (i) once deposited, the antioxidant remains attached to the fibres by electronic interactions and hydrogen bonding, i.e., wear-off is limited; and (ii) once deposited the antioxidant does not undergo any chemical changes, i.e., does not lose its antioxidant activity.

Analysis was performed by the $ABTS^{\bullet+}$ decolourisation assay as shown in Table 5, on the basis of a specific calibration for the compounds under analysis in the $ABTS^{\bullet+}$ decolourisation assay based on a calibration obtained for PST (Figure S3 in Supplementary Materials).

Table 5. Amount of antioxidants deposited on fabric determined by $ABTS^{\bullet+}$ decolourisation assay.

Entry	Fabric	Sample (10 mg)	Amount of Pine Tannin Deposited on 10.0 mg Fabric [μg]	Amount of Pine Tannin Deposited on 10.0 mg Fabric [Mean Value ± sd in μg]
1	**PST-sW1**_cotton_ H_2O mechanical	1	0.25	0.24 ± 0.20
2	**PST-sW1**_cotton_ H_2O mechanical	2	0.26	
3	**PST-sW1**_cotton_ H_2O mechanical	3	0.49	
4	**PST-sW1**_cotton_ H_2O mechanical	4	0.13	
5	**PST-sW1**_cotton_ H_2O mechanical	5	0.09	
6	**PST-sW1**_cotton_ HDL_mechanical	1	0.25	0.23 ± 0.02
7	**PST-sW1**_cotton_ HDL_mechanical	2	0.21	
8	BHT cotton_ H_2O	1	0.27	0.20 ± 0.07
9	BHT cotton_ H_2O	2	0.17	
10	BHT cotton_ H_2O	3	0.22	
11	BHT cotton_ H_2O	4	0.15	
12	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyl-phenyl)propanoate cotton_ H_2O	1	0.15	0.14 ± 0.01
13	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyl-phenyl)propanoate cotton_ H_2O	2	0.14	
14	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyl-phenyl)propanoate cotton_ H_2O	3	0.14	
15	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyl-phenyl)propanoate cotton_ H_2O	4	0.13	

As can be seen in Table 5, the values obtained for the measurements confirm a nonhomogeneous tannin deposition onto the fabrics as it could be expected based on the chosen deposition method, the industrial launderometer process used to treat the textiles with the chosen pine tannin under the various conditions. Hence, this non-homogenous deposition could well explain the large error observed in the antioxidant activity measurements (see Table 2). On the contrary, the deposition of commercial antioxidant species carried out manually is, as expected, homogenous.

4. Conclusions

Pine tannins and commercial antioxidant species were deposited on model fabrics. A dedicated test method, based on the ABTS assay, was developed to determine deposition efficiency and homogeneous distribution of the antioxidant species on the fabric. The developed procedure could be also successfully applied to measure the residual antioxidant activity of the species deposited on fabrics. A known source of odour is autoxidation of residual sebum on fabric, leading to generation of an array of odoriferous compounds [20]. Antioxidants hold thus a promise for mitigating malodour on fabrics, a top unmet consumer need around the globe.

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/10/18/6213/s1, Figure S1: Structures of synthetic phenolic antioxidants; Figure S2: $ABTS^{\bullet+}$ decolorization assay before and after addition of M*t*BHPP (1 mg/mL in ethanol); Figure S3: **PST-sW1** calibration plot for evaluation of amount of active tannin deposited on fabric.

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