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Characterisation and tanning effects of purified chestnut and sulfited quebracho extracts

Silvia Conca¹, Vanessa Gatto¹, Riccardo Samiolo¹, Samuele Giovando², Andrea Cassani², Elisa Tarabra² and Valentina Beghetto^{1,3,4*} 

Abstract

Vegetable tannins are environmentally friendly tanning agents. However, they generally impart a dark colour to the tanned leather and highly contribute to the organic load in wastewaters. In this study, we employed a purification protocol separately on chestnut tannin (CT) and sulfited quebracho tannin (QT) to obtain the purified fractions (PCT and PQT). These samples were characterised by GPC, ¹H NMR, ¹³C NMR, FT-IR, and HPLC–DAD techniques and applied for tanning tests. Through the purification process, non-tannin components and smaller molecules such as gallic acid, glucopyranose, and catechin were effectively removed from CT and QT, which consequently led to the reduced moisture content, pH value, and lighter colour of purified fractions. The crust leathers processed with PCT and PQT showed desirable light shades. Moreover, the organic loads in PCT and PQT tanning wastewater were reduced by 13.5% and 19.1%, respectively, when compared to those in traditional CT and QT tanning wastewater. Additionally, the physical and mechanical characteristics of crust leathers processed with PCT and PQT were comparable to those processed with CT and QT. Thus, purification of vegetable tannins may serve as a feasible strategy for producing light-colored vegetable-tanned leather while minimizing organic pollutant discharge during the vegetable tanning process.

Keywords Purification, Chestnut, Quebracho, Vegetable tanning, Biomass, Leather

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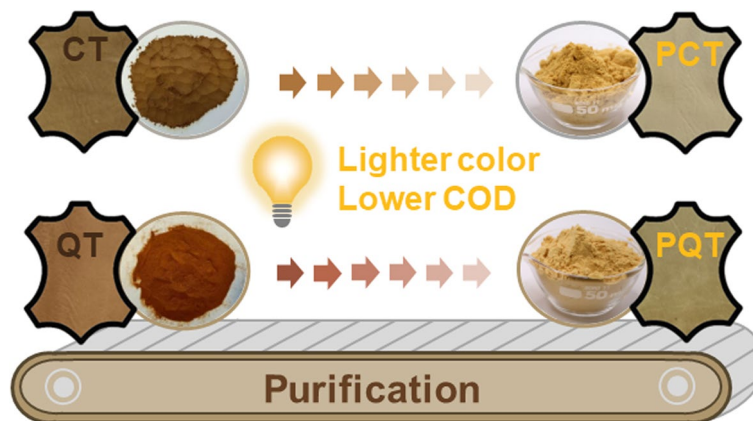
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Graphical Abstract



1 Introduction

Leather processing, one of the oldest activities of mankind, involves the transformation of food by-products (hides) into useful and valuable goods (leather) [1–4]. Throughout history, this fundamental skill has evolved into an intricate art form that produces everyday objects and valuable products for renowned fashion designers.

Currently, over 85% of the leather products are tanned with Cr(III) salts to produce “wet blue” due to its superior leather quality, cost-effectiveness, versatility, and replicability. The remaining 15% of the market employs alternative chrome-free metal salts (such as aluminium, titanium, or zirconium salts) or metal-free tanning agents like aldehydes, natural or synthetic tannins. These alternatives result in the production of chrome-free leather [5–8]. However, the use of chrome salts generates high quantities of chromium containing solid sludge, thereby leading to high disposal costs and environmental burden [4, 9–14]. Of every 1000 kg of salted bovine hides delivered to the tannery, only 250–300 kg is transformed into finished leather while the remaining 700–750 kg is discarded as waste, resulting in approximately 15–50 m³ of water effluents containing about 250 kg chemical oxygen demand (COD) and 100 kg biological oxygen demand (BOD) [15]. These statistics, coupled with stringent European regulations that prioritize environment protection, have gradually promoted the development and adoption of novel sustainable chrome-free and high exhaustion tanning systems for leather production [9, 13, 16]. Nevertheless, it should be noted that most chrome-free tanning agents also face increasing restrictions under REACH regulation due to their adverse impact on human health even though they don’t release chromiums. Moreover, the chrome-free leather usually exhibits inferior

physical–mechanical properties [8]. Thus far, the choice between chrome and chrome-free leather involves complex technical, economic, and political considerations that continue to support chrome tanning as the dominant technology for leather production [5, 17].

In the past decade, vegetable biomass has emerged as a pivotal research topic in this field, as evidenced by numerous publications investigating its potential as tanning agents [18–23]. Vegetable tannins are regarded as a valuable alternative to chrome-free leather due to their natural origin and absence of hazardous substances. However, the utilization of vegetable tannins is currently limited due to the inferior physical and mechanical characteristics as well as higher production costs of vegetable-tanned leather. To enhance the tanning effects and improve the overall physical, mechanical, and organoleptic characteristics of vegetable-tanned leather, it is a common practice to combine vegetable tannins with aluminium salts for tanning. Although this approach improves hydrothermal stability and organoleptic properties of the resultant leather, it compromises the leather versatility and environmental sustainability [24–26]. The substantial amount of vegetable tannin used (up to 40 wt% based on weight of processed leather) negatively affects both the colour of tanned leather and COD in wastewater [27]. Thus, there is a great interest in exploring new processes that can simultaneously lighten the colour and enhance the tanning efficiency of vegetable tannin, mitigating their environmental impact on wastewater.

Therefore, in this work, chestnut tannin (CT) and sulfited quebracho tannin (QT) were subjected to a purification protocol to obtain purified tannins (PCT and PQT). These samples were characterised using gel

permeation chromatography (GPC), nuclear magnetic resonance spectroscopy (NMR), Fourier-transform infrared spectroscopy (FT-IR), and high-performance liquid chromatography (HPLC). The tannin versus non-tannin ratio, pH, moisture and ash content were determined. Additionally, tanning trials were performed on depickled bovine pelts to investigate the tanning effects and environmental impacts of PCT and PQT.

2 Experimental section

2.1 Materials

The CT (chestnut tannin derived from *Castanea Sativa*) and QT (sulfitated quebracho tannin derived from *Schinopsis Lorentzii*) were supplied by Silvateam (San Michele di Mondovì, Italy). The purified tannins (PCT and PQT), the residual fractions (RCT and RQT) and bovine depickled pelts were also supplied by Silvateam (San Michele di Mondovì, Italy). Solvents and chemicals were purchased from Sigma Aldrich (Italy) and used without further purification.

2.2 Structural characterizations

2.2.1 Moisture content

The drying oven method is a thermogravimetric technique (loss on drying) in which the sample undergoes controlled desiccation for a specified duration of 4 h at a constant temperature of $102\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$. The moisture content was determined by weighing the sample before (M1) and after (M2) drying, and subsequently calculating the ratio of weight loss (M1-M2) to the initial sample weight, according to Eq. 1:

$$M (\%) = \frac{M1 - M2}{M1} \times 100 \quad (1)$$

2.2.2 Ash content

The samples (about 500 mg) were placed into a crucible and subjected to heating at $550\text{ }^{\circ}\text{C}$ in a muffle furnace. The ash content (%) was determined by calculating the difference between the weight before (A1) and after (A2) heating, divided by the initial weight of the sample, according to Eq. 2:

$$\text{Ash} (\%) = \frac{A1 - A2}{A1} \times 100 \quad (2)$$

2.2.3 Tannin content and pH value

The content of tannin and insoluble component in each sample was determined using the standard method (ISO 14088:2020).

The pH value was measured using a pH-meter (Hach Lange, mod. SensiON+ PH 3) on a 10% dry matter colloidal solution.

2.2.4 GPC analysis

The number-average molecular weight (M_n) of all samples was determined using an Agilent 1260 Infinity II chromatograph equipped with a UV detector (260 nm). A HP-PL gel $5\text{ }\mu\text{m}$ Mixed-D column protected with a PL gel $5\text{ }\mu\text{m}$ guard column (Agilent) was employed. Tetrahydrofuran (THF) served as eluent, and a calibration curve was established using polystyrene standards. The environmental included a flow rate of 1 mL/min and a column temperature of $30\text{ }^{\circ}\text{C}$. The extracts were derivatized according to a standard literature procedure prior the analysis [28].

2.2.5 NMR analysis

The ^1H NMR and ^{13}C NMR spectra were acquired using a Bruker UltraShield 400 spectrometer operating at frequencies of 400.0 and 101.0 MHz, respectively. Samples weighing precisely 100.0 mg were dissolved in 600 μL of deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$).

2.2.6 FT-IR analysis

The FT-IR spectra (1 wt% tannin/KBr) were recorded using a Perkin-Elmer Spectrum-One spectrophotometer, covering the range from 4000 to 450 cm^{-1} with 32 scans and a resolution of 4 cm^{-1} .

2.2.7 HPLC analysis

The tannins were analysed by HPLC at 260 nm using a Perkin Elmer Flexar LC system, which consisted of the following parts: a Flexar PDA Plus Detector (diode array detector), Flexar Peltier LC Autosampler, Flexar Peltier LC Column Oven, a Flexar LC Quaternary Pump, and a Flexar Solvend Manger 5-CH Degaser. The analysis was performed on a Waters C18 XSelect[®] HSS T3 column ($3.5\text{ }\mu\text{m}$ particle size, $4.6\text{ mm} \times 150\text{ mm}$) with an accompanying guard column (20 mm) made of the same material. Identification of different compounds was achieved using commercially available standards.

2.3 Tanning tests

Tanning tests were carried out on depickled bovine pelts in $25\text{ cm} \times 20\text{ cm}$ (approximately 300 g, with a thickness of 1.3–1.4 mm). The pelts were placed in a drum containing 100%wt water (based on the weight of pelts), NaCl (7°Bè), and 40%wt of tanning agents. Then, the hides were left to rotate overnight until reaching pH 4–5 (with basification using NaHCO_3 if necessary). The tanned hides were dried, and their Ts values (IULTCS/IUP 16,

2015) were evaluated. A conventional post-tanning process was adopted to obtain the crust leathers.

2.4 Physical–mechanical and organoleptic properties and environmental impact

The physical–mechanical properties (including thickness, tensile strength, tearing load, and elongation at break) of crust leathers were determined according to IUP 6 (ISO 3376:2020) and IUP 8 (ISO 3377–2, 2016). Organoleptic characteristics such as colour, fullness, resistance to UV and Xe light, as well as heat stability were assessed through manual and visual examination. Each property was assigned a score ranging from 1 to 5, with higher scores indicating better performance. The COD of wastewater after tanning processes was analysed using the APAT CNR IRSA 5130 method.

3 Results and discussion

Vegetable tannins are naturally occurring water-soluble polyphenolic compounds found in various plant parts such as tree barks, stems, leaves, seeds, and roots, as well as nuts, fruits, spices, and herbs. These compounds typically have molecular weights ranging from 500 to 3,000 Da and can be mainly classified into hydrolysable tannins and condensed tannins [29–31]. Hydrolysable tannins consist of a carbohydrate core (e.g. glucose) esterified with gallic acid (gallotannins) or ellagic acid (ellagitannins), which can be easily hydrolysed in the presence of weak acids or bases. In contrast, condensed tannins (known as proanthocyanidins) are composed of flavonoid oligomers where the flavonoid units (mainly flavan-3-ols) are linked through C4–C6 or C4–C8 bonds (Fig. 1). Condensed tannin production accounts for over 90% of global commercial tannin output [29, 31]. This study analysed commercially available hydrolysable tannin extracted

from *Castanea sativa* tree and modified condensed tannin derived from *Schinopsis Lorentzii* (Fig. 1).

Chestnut extracts are hydrolysable tannins comprising a mixture of castalin, vescalalin, castalagin and vescalagin, along with other small molecules such as gallic acid and glucopyranose [32–34]. These ellagitannins are characterized by a glucose core esterified with at least one hexahydroxydiphenyl acidic moiety, which is formed through oxidative coupling between two gallic acid units [35].

Quebracho extracts are a mixture of proanthocyanidins (i.e. flavan-3-ol oligomers or high molecular weight polymers) and traces of smaller molecules such as ellagic or gallic acid [36, 37]. Due to their extremely low water-solubility, commercially available quebracho extracts are often sulfited using NaHSO_3 to improve their solubility (Scheme 1) [38–41].

3.1 Characterization of tannins before and after purification

3.1.1 Tannic content, pH, moisture, and ash content

The CT and QT samples underwent a purification process to obtain the PCT and PQT fractions, as well as the residual RCT and RQT fractions. The tannin content, ratio of tannin to non-tannin (T/nT), moisture content, pH value, ash content, and M_n of CT, QT and their purified and residual fractions were determined and are presented in Table 1. The T/nT values of PCT and PQT were nearly twice compared to those of CT and QT, possibly owing to the reduced concentration of non-tannin molecules present in the purified fractions. In contrast, RCT and RQT showed remarkably low T/nT ratios and substantial ash contents because of the presence of abundant non-tannin molecules such as sugars and gallic acid. PCT and PQT exhibited relatively low moisture contents, which can be ascribed to the increased benzene rings

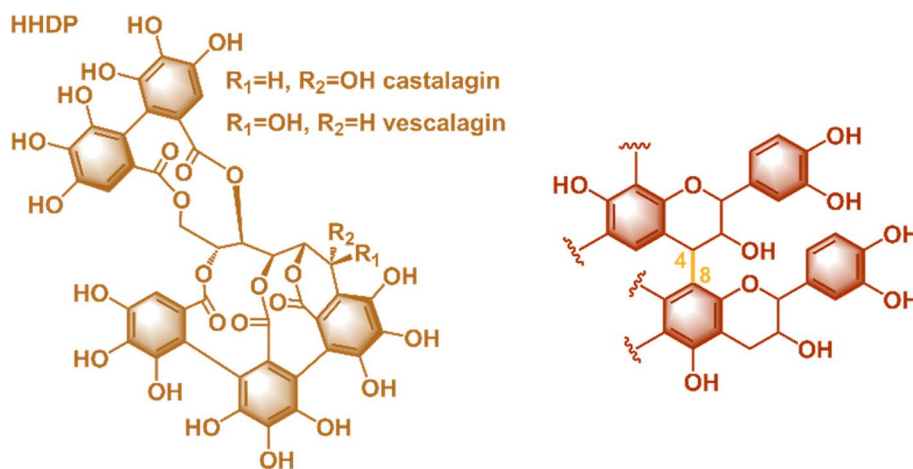
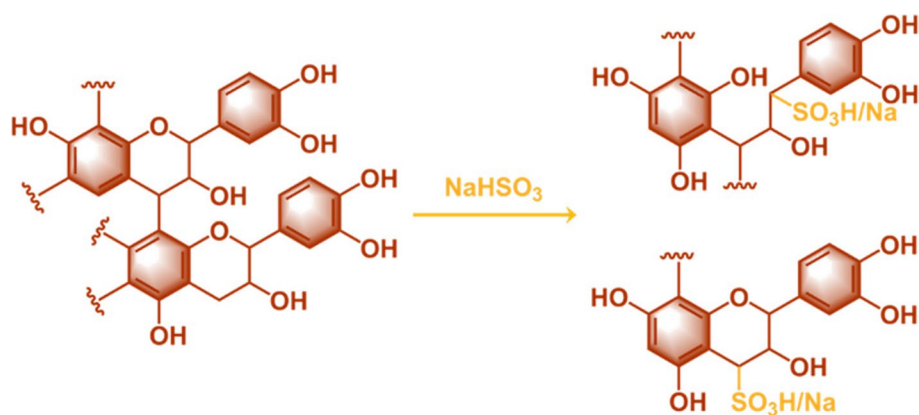


Fig. 1 Main specie of chestnut and quebracho tannins



Scheme 1 Sulfitation of quebracho tannin

Table 1 Chemical composition of CT and QT, as well as their purified and residual fractions

Sample	Color	Tannin content (%)	T/nT ^a	Moisture content (%)	pH	Ash content (%)	M _n
CT	Brown	40.2	4.6	5.0	3.5	0.98	1,350
PCT	Yellow	83.1	8.3	4.0	3.3	1.60	680
RCT	Brown	52.0	1.2	4.3	3.6	5.06	530
QT	Red-brow	79.4	5.2	5.3	4.6	6.52	1,850
PQT	Yellow	87.8	11.2	3.9	4.5	3.90	780
RQT	Brown	54.3	1.4	4.5	5.2	29.13	650

^a Ratio of tannin to non-tannin

with hydrophobicity. Meanwhile, the observed low pH values of the PCT and PQT may be attributed to the dissociation of phenolic hydroxyl groups. It is noteworthy that the PCT and PQT had a remarkably lighter colour compared to CT and QT (Fig. 2), which is expected to be highly beneficial for leather tanning. Regarding insoluble molecules, only negligible amounts were detected in all tannin extracts (<1 mg/mL). The M_n of all samples fell within the range of 500–3,000, which is deemed suitable for leather tanning. Additionally, the colloidal solution of purified tannins was stored in a dark and cool environment, showing no formation of precipitates over a period of 4–6 months, thereby demonstrating their good stability.

3.1.2 NMR analysis

The chemical structure of CT and its purified and residual fractions was analysed using ¹H and ¹³C NMR spectroscopy (Fig. 3). The ¹H NMR spectra of CT can be divided into three main regions. Signals observed in the chemical shift range between 3.0 and 5.5 ppm were ascribed to the CH and CH₂ groups, indicating the presence of carbohydrates such as glucopyranose and the aliphatic moiety of castalagin and vescalagin. The characteristic aromatic moiety of the polyphenols was

detected between 6.0 and 7.5 ppm, while signals above 7.5 ppm corresponded to the broad -OH signal from phenolic compounds. Moreover, two signals at 6.93 ppm and 7.45 ppm were attributed to gallic acid and ellagic acid, respectively. The ¹³C NMR spectra also revealed three main sets of signals, in accordance with previous literature [32, 42]. Carbon signals ranging from 54.0 to 78.0 ppm corresponded to the glucopyranose ring and aliphatic carbons of castalagin and vescalagin. Signals between 100.0 and 150.0 ppm were ascribed to the aromatic carbon atoms. Notably, characteristic carbon signals related to hexahydroxydiphenyl and trigalloyl moiety were identified around 110 ppm. Aromatic carbon atoms bonded to the -OH functional group resonated between 140.0 and 150.0 ppm, together with carbonyl ester groups at around 170.0 ppm. These findings demonstrated CT is a typical ellagitannin.

In ¹³C NMR spectrum of PCT, glucopyranose signals were identified at chemical shifts of 101.9 (a), 76.8 (b), 73.3 (c), 69.9 (d), 68.4 (e) and 65.2 (f) ppm (Fig. 3) [32]. As for the residual fractions, RCT was mainly composed of gallic acid as evidenced by its characteristic peak at 6.93 ppm in the ¹H NMR spectrum. These findings were further supported by corresponding peaks observed at chemical shifts of 167.8 (1), 145.6 (4,6), 138.1 (5), 120.8



Fig. 2 Powders of CT/PCT and QT/PQT

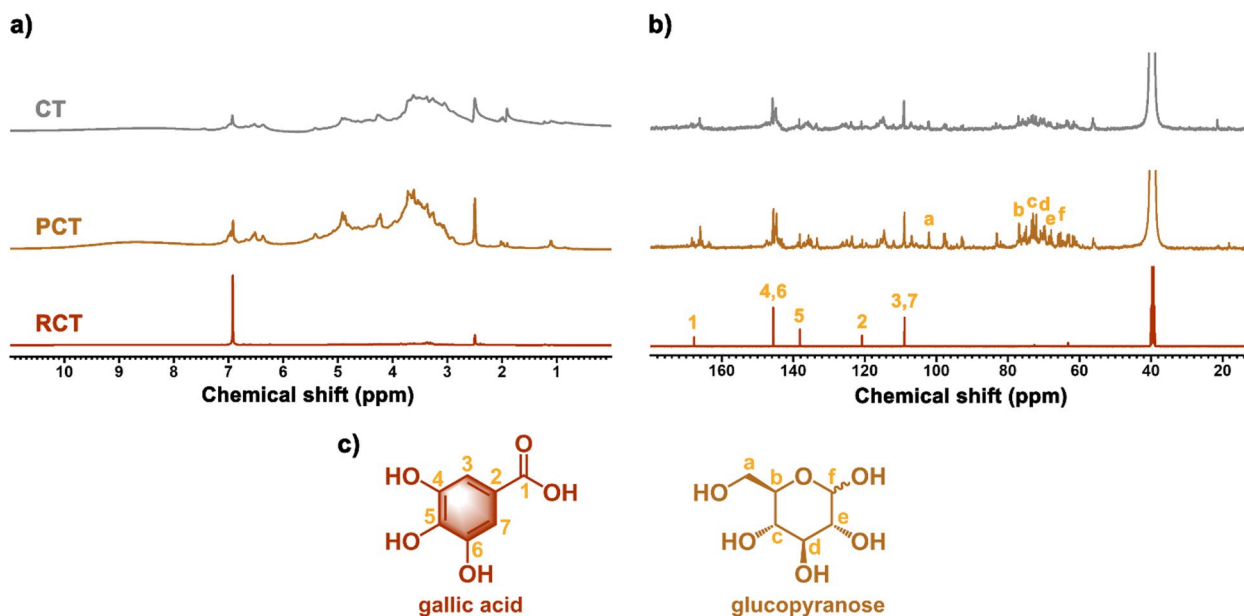


Fig. 3 ¹H NMR (a) and ¹³C NMR (b) of CT and its purified (PCT) and residual fractions (RCT); The chemical structure of gallic acid and glucopyranose structure (c)

(2), and 108.9 (3,7) ppm in its ¹³C NMR spectrum [43]. Interestingly, RCT, obtained as counterpart to PCT, mainly composed of gallic acid, thus confirming that PCT was obtained by the effective separation of lower molecular weight molecules (RCT) from CT through this purification process.

As for QT, the ¹H NMR spectrum (Fig. 4) exhibited three main proton regions, indicating diverse proton types. Numerous signals were observed within the range of 2.9 to 5.7 ppm, corresponding to CH and CH₂ groups attributed to the presence of carbohydrates ring (C ring). In the aromatic region (6.0–7.7 ppm), a broad peak was

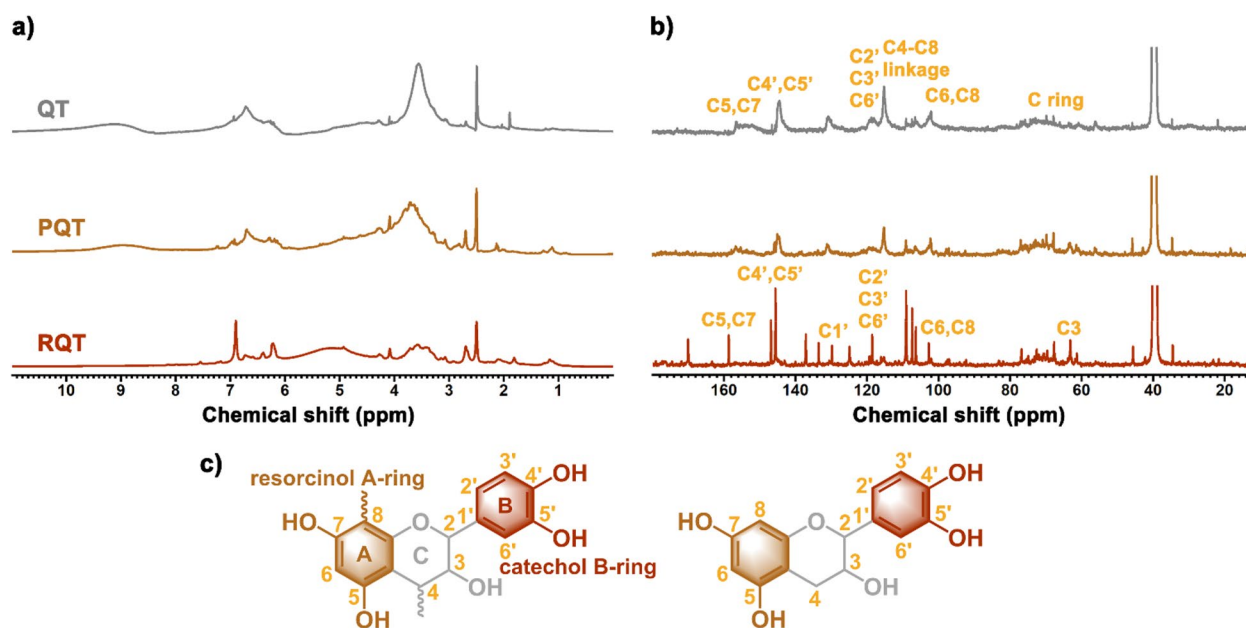


Fig. 4 ¹H NMR (a) and ¹³C NMR (b) of QT and its purified (PQT) and residual fractions (RQT); The chemical structure of QT and catechin (c)

evident, representing aromatic protons of A and B rings, while between 8.4 and 10.5 ppm, a broad peak emerged due to the phenolic -OH functional group. In the ¹³C NMR spectra, all peaks have been assigned, confirming the flavonoid structure of QT predominantly composed of proanthocyanidins (about 95%) [36]. Specifically, signals in the chemical shift range of 61.0 to 77.0 ppm corresponded to the carbohydrate moiety (C ring), while those between 116.3 and 119.9 ppm and at 130.6 ppm (C2', C3', C6' and C1') together with the strong signal at 144.0 ppm (C4', C5') confirmed the presence of the catechol B-ring [44]. The strong signal at 115.1 ppm indicated the occurrence of a catechin dimer in QT extracts, as evidenced by the formation of a C4-C8 bond. The broad spectra bands observed between 150.0 and 160.0 ppm corresponded to C5 and C7 bonded to the -OH functional group, whereas the peak around 102.0 ppm (C6, C8) indicated the presence of the resorcinol structure of the A ring. Moreover, the signal at 55.8 ppm may be attributed to the methoxy groups present in lignin fragments [45, 46].

As shown in Fig. 4, the ¹H and ¹³C NMR spectra of PQT exhibited more resolved peaks, indicating the effective removal of smaller molecules through the purification protocol. The presence of lower molecular weight substances in RQT fraction was confirmed by their highly resolved peaks in the ¹³C NMR spectra, which was further supported by average molecular weight analysis presented in Table 1. Notably, a characteristic peak at 115.1 ppm corresponding to oligomeric species was absent in RQT fraction, confirming their composition of

lower molecular weight compounds such as gallic acid and catechin (158.8, 147.1, 129.5, 118.3, 102.8, 79.4, 63.1, 24.4 ppm) [43, 47].

In general, the NMR analysis confirmed the GPC data and provided additional information on the composition of each analysed fraction. In particular, the purification methodology demonstrated notable efficacy in removing small molecules such as gallic acid, glucopyranose, and catechin, thereby enriching oligomeric structures within vegetable tannins.

3.1.3 FT-IR analysis

The FT-IR spectra of CT and QT, as well as their purified and residual fractions, are presented in Fig. 5. In the FT-IR spectra of CT sample, within the 3400–3000 cm⁻¹ region, the presence of OH stretching vibration was observed. Additionally, CH and CH₂ stretching vibrations originating from aliphatic group in CT were identified around 2900 cm⁻¹. A medium-strong band at 1739 cm⁻¹, characteristic of hydrolysable tannins and attributed to the C=O stretching of esters derived from gallic acid, was evident in both CT and PCT spectra. Conversely, RCT spectrum exhibited typical bands associated with gallic acid, and specifically a signal at 1661 cm⁻¹ corresponded to the C=O stretching. The region ranging from 1614 to 1450 cm⁻¹ displayed similarities across all spectra and corresponded to the C=C aromatic stretching. As for the QT sample, the CH and CH₂ stretching vibrations originating from the C-ring were observed around 2900 cm⁻¹. The presence of the catechin moiety in both

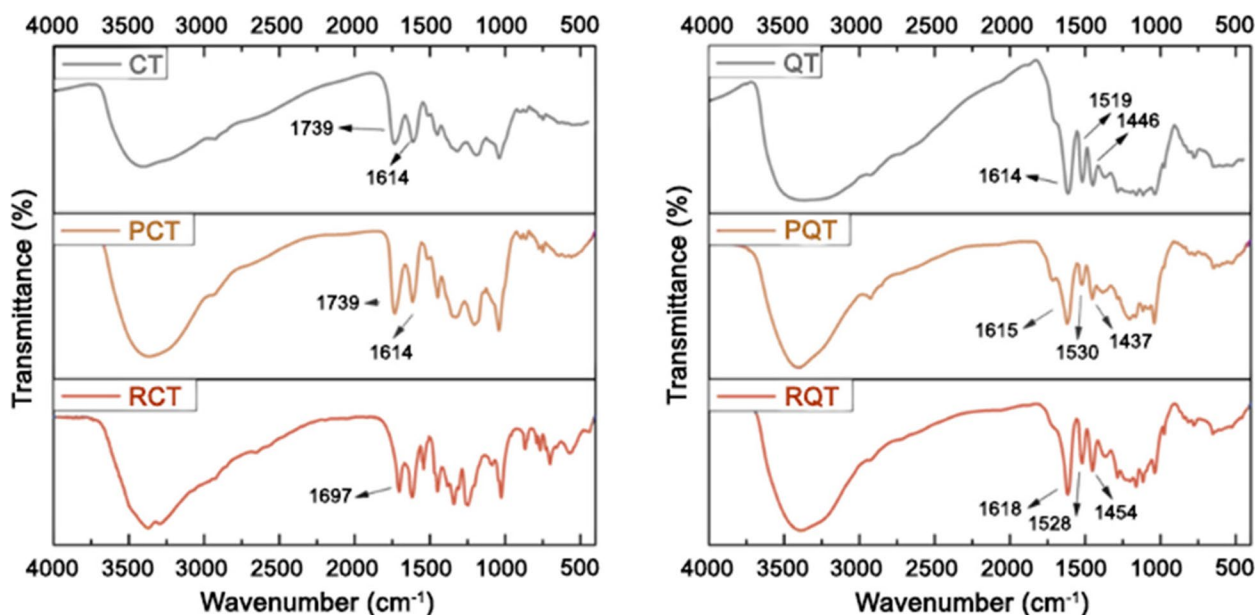


Fig. 5 FT-IR spectra of CT (left) and QT (right), as well as their purified and residual fractions

PQT and RQT was confirmed by strong bands observed at 1614 cm^{-1} , 1519 cm^{-1} , and 1446 cm^{-1} , corresponding to the C=C aromatic stretching of condensed tannins [35]. Thus, FT-IR analysis further confirmed that the purification process did not modify the primary structure of tannin but only removed smaller molecules.

3.1.4 HPLC analysis

HPLC chromatogram of CT (Figure S1) confirmed the presence of low molecular weight substances, including castalagin, vescalagin, and gallic acid. Remarkably weak signal for gallic acid in PCT provided evidence for the effective removal of lower molecular weight compounds during the purification process. However, both castalagin and vescalagin were retained in PCT. HPLC chromatogram of QT exhibited greater complexity, with only gallic acid being identified (Figure S2). Nevertheless, it was observed that the purification process partially removed gallic acid for the much weaker signal of gallic acid in PQT.

3.2 Tanning tests, physical and organoleptic properties of tanned leather

The tanning effects of CT and QT, as well as their purified products (PCT and PQT), were investigated through tanning tests. As shown in Table 2, the tanning performance of PCT and PQT was found to be comparable to that of CT and QT in consideration of T_s values and physical mechanical characteristics of crust leathers, demonstrating that the purification process has little effect on the

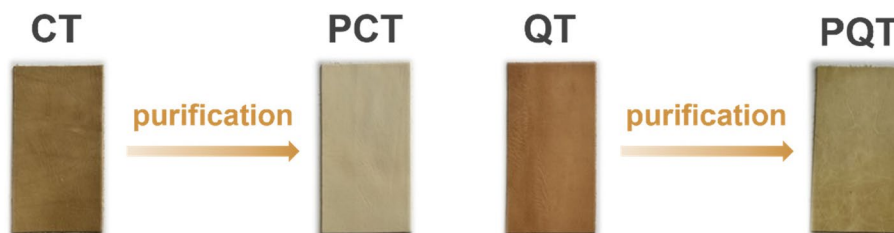
tanning properties of vegetable tannins. The tearing load of all the crust leathers exceeded the minimum requirement for upholstery leather, which follows a common rigid characteristic of vegetable tanned leather. However, the tearing load in PCT and PQT groups was lower compared to the CT and QT groups, indicating that these purified products may have enhanced softness of leather [9]. Notably, the purification process offers clear benefit by effectively reducing COD by 13.5% and 19.1% in wastewater from PCT and PQT tanning process respectively, probably due to the removal of lower molecular weight substances in vegetable tannins. Although further research is required to elucidate the tanning mechanism of different extracts reported in this study, it can be inferred that the PCT and PQT pose higher reactivity towards collagen, resulting in improved fixation of tannin in leather and thus reducing COD in wastewater. In addition, the crust leathers obtained using PCT and PQT exhibited noticeably lighter colour, which is conducive to the subsequent dyeing effect of leather (Fig. 6).

4 Conclusions

The PCT and PQT samples, derived from CT and QT through purification process, were subjected to characterization using GPC, NMR, FT-IR, and HPLC techniques and subsequent tanning of depicked bovine pelts. The purification process effectively preserved the primary structure of the two tannins while selectively removing non-tannin compounds or smaller molecular components such as gallic acid, glucopyranose, and

Table 2 Physical–mechanical, organoleptic properties of tanned leathers and COD in tanning wastewater

Sample	CT	PCT	QT	PQT	Upholstery leather
<i>Physical–mechanical properties</i>					
Ts (°C)	61 ± 2	57 ± 2	80 ± 2	78 ± 2	> 75
Thickness (mm)	1.23 ± 0.1	1.28 ± 0.1	1.42 ± 0.1	1.51 ± 0.1	
Tensile strength (N/mm²)	19.95 ± 0.9	13.25 ± 1.2	14.27 ± 1.4	11.80 ± 0.3	> 8
Tearing load (N)	245 ± 4	170 ± 7	202 ± 3	181 ± 4	> 40
Elongation at break (%)	20	18	29	24	< 80
<i>Organoleptic properties</i>					
Colour	3	4	3	5	
Fullness	4	5	4	5	
Heat fastness	4	3	2	2	
<i>Environmental impact</i>					
COD (g/L)	60.1 ± 0.8	52.0 ± 0.8	70.5 ± 0.8	57.0 ± 0.8	

**Fig. 6** The colour of tanned leathers

catechin. The leathers processed with PCT and PQT exhibited lighter colour but comparable organoleptic and physical–mechanical properties compared to those processed with CT and QT. Notably, the COD in wastewater by utilizing PCT and PQT as tanning agent was reduced, probably benefited from the removal of smaller molecules with poor fixation ability with collagen. Therefore, a rational purification approach for vegetable tannins can not only lighten the colour of vegetable-tanned leather but reduce the organic load in vegetable tanning wastewater, which is worthy of further research in the future. This study proposes a straightforward and convenient strategy to promote high-quality development of vegetable tannins.

Abbreviations

COD	Chemical oxygen demand
CT	Chestnut tannin
FT-IR	Fourier-transform infrared
GPC	Gel permeation chromatography
HPLC	High performance liquid chromatography
QT	Sulfited quebracho tannin
NMR	Nuclear magnetic resonance
PCT	Purified chestnut tannin
PQT	Purified sulfited quebracho tannin
RCT	Residual chestnut tannin
RQT	Residual sulfited quebracho tannin

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s42825-024-00171-9>.

Supplementary Material 1.

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Not applicable.

Authors' contributions

Silvia Conca, Valentina Beghetto, Vanessa Gatto: Conceptualization, Investigation, Writing – original draft, Writing—review & editing, Samuele Giovando, Andrea Cassani, Elisa Tarabra: Data curation, Writing—review & editing, Riccardo Samiolo: Data curation, Formal analysis, Samuele Giovando, Valentina Beghetto: Reviewing, Formal analysis, Valentina Beghetto: Supervision, Formal analysis.

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Availability of data and materials

All data are included in this published article.

Declarations**Ethics approval and consent to participate**

Written informed consent is obtained from all the participants prior to the publication of this study.

Consent for publication

The author confirms: that the work described has not been published before; that it is not under consideration for publication elsewhere; that its publication has been approved by all co-authors; that its publication has been approved (tacitly or explicitly) by the responsible authorities at the institution where the work is carried out.

Competing interests

Valentina Beghetto is a member of the editorial board of *Collagen and Leather*, and was not involved in the editorial review, or the decision to publish this article.

All authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Joseph K, Nithya N. Material flows in the life cycle of leather. *J Cleaner Prod.* 2009;17:676–82. <https://doi.org/10.1016/j.jclepro.2008.11.018>.
- Rosu L, Varganici CD, Crudu AM, Rosu D, Bele A. Ecofriendly wet-white leather vs. conventional tanned wet-blue leather. A photochemical approach. *J Cleaner Prod.* 2018;177:708–20. <https://doi.org/10.1016/j.jclepro.2017.12.237>.
- Leather RR. Ullmann's encyclopedia of industrial chemistry. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA; 2015. p. 621–63.
- Covington AD. Tanning chemistry: the science of leather. Cambridge: Royal Society of Chemistry; 2009.
- Hassan MM, Harris J, Busfield JJC, Bilotti E. A review of the green chemistry approaches to leather tanning in imparting sustainable leather manufacturing. *Green Chem.* 2023;25:7441–69. <https://doi.org/10.1039/D3GC02948D>.
- Sabatini F, Corsi I, Ceccarini A, Brillanti M, Colombini MP, Bonaduce I. Pyrolysis gas chromatography mass spectrometry: a promising tool for disclosing metal-free tanning agents used in leather industry. *J Anal Appl Pyrolysis.* 2023;169:105803. <https://doi.org/10.1016/j.jaap.2022.105803>.
- Chen W, Chen Z, Long Z, Shan Z. Development of aldehyde and similar-to-aldehyde tanning agents. *Text Res J.* 2021;92:3387–97. <https://doi.org/10.1177/00405175211023813>.
- Facchin M, Gatto V, Samiolo R, Conca S, Santandrea D, Beghetto V. May 1,3,5-Triazine derivatives be the future of leather tanning? A critical review. *Environ Pollut.* 2024;345:123472. <https://doi.org/10.1016/j.envpol.2024.123472>.
- Beghetto V, Agostinis L, Gatto V, Samiolo R, Scrivanti A. Sustainable use of 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride as metal free tanning agent. *J Clean Prod.* 2019;220:864–72. <https://doi.org/10.1016/j.jclepro.2019.02.034>.
- Qiang T, Gao X, Ren J, Chen X, Wang X. A chrome-free and chrome-less tanning system based on the hyperbranched polymer. *ACS Sustainable Chem Eng.* 2016;4:701–7. <https://doi.org/10.1021/acssuschemeng.5b00917>.
- Gatto V, Conca S, Bardella N, Beghetto V. Efficient triazine derivatives for collagenous materials stabilization. *Materials.* 2019;14:3069. <https://doi.org/10.3390/ma14113069>.
- Sole R, Taddei L, Franceschi C, Beghetto V. Efficient chemo-enzymatic transformation of animal biomass waste for eco-friendly leather production. *Molecules.* 2019;24:2979. <https://doi.org/10.3390/molecules24162979>.
- Beghetto V, Gatto V, Conca S, Bardella N, Scrivanti A. Polyamidoamide dendrimers and cross-linking agents for stabilized bioenzymatic resistant metal-free bovine collagen. *Molecules.* 2019;24:3611. <https://doi.org/10.3390/molecules24193611>.
- Liu K, Shi Z, Zhou S. Reduction of hexavalent chromium using epigallocatechin gallate in aqueous solutions: kinetics and mechanism. *RSC Adv.* 2016;6:67196–203. <https://doi.org/10.1039/C6RA02131J>.
- Best Available Techniques (BAT) Reference. Tanning of hides and skins 2013. <https://eippcb.jrc.ec.europa.eu/reference/tanning-hides-and-skins-0>. Accessed 12 Dec 2023.
- Lofrano G, Meriç S, Zengin GE, Orhon D. Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: a review. *Sci Total Environ.* 2013;461–462:265–81. <https://doi.org/10.1016/j.scitotenv.2013.05.004>.
- China CR, Maguta MM, Nyadoro SS, Hilonga A, Kanth SV, Nkai KN. Alternative tanning technologies and their suitability in curbing environmental pollution from the leather industry: a comprehensive review. *Chemosphere.* 2020;254:126804. <https://doi.org/10.1016/j.chemosphere.2020.126804>.
- Scelsi E, Angelini A, Pastore C. Deep eutectic solvents for the valorisation of lignocellulosic biomasses towards fine chemicals. *Biomass.* 2021;1(1):29–59. <https://doi.org/10.3390/biomass1010003>.
- Merino D, Athanassiou A. Thermomechanical plasticization of fruits and vegetables processing byproducts for the preparation of bioplastics. *Adv Sustainable Syst.* 2023;7:2300179. <https://doi.org/10.1002/adsu.20230179>.
- Beghetto V, Gatto V, Conca S, Bardella N, Buranello C, Gasparetto G, Sole R. Development of 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride cross-linked carboxymethyl cellulose films. *Carbohydr Polym.* 2020;249:116810. <https://doi.org/10.1016/j.carbpol.2020.116810>.
- Sole R, Buranello C, Di Michele A, Beghetto V. Boosting physical-mechanical properties of adipic acid/chitosan films by DMTMM cross-linking. *Int J Biol Macromol.* 2022;209:2009–19. <https://doi.org/10.1016/j.ijbiomac.2022.04.181>.
- Koochakzadeh A, Sabaghian M. Tannin characterization and sourcing in historical leathers through FTIR spectroscopy and PCA analysis. *Collagen Leather.* 2023;5:21. <https://doi.org/10.1186/s42825-023-00128-4>.
- Falcao L, Araujo MEM. Vegetable tannins used in the manufacture of historic leathers. *Molecules.* 2018;23(5):1081. <https://doi.org/10.3390/molecules23051081>.
- China CR, Hilonga A, Nyadoro SS, Schroeppfer M, Kanth SV, Meyer M, Njai KN. Suitability of selected vegetable tannins traditionally used in leather making in Tanzania. *J Clean Prod.* 2020;251:119687. <https://doi.org/10.1016/j.jclepro.2019.119687>.
- Pizzi A, Simon C, George B, Perrin D, Triboulet MC. Tannin antioxidant characteristics in leather versus leather light stability: Models. *J Appl Polym Sci.* 2004;91:1030–40. <https://doi.org/10.1002/app.13047>.
- Krishnamoorthy G, Ramamurthy G, Sadulla S, Parvathaleswara Sastry T, Mandal AB. Click chemistry approach to conventional vegetable tanning process: accelerated method with improved organoleptic properties. *Environ Sci Pollut Res.* 2014;21:10678–85. <https://doi.org/10.1007/s11356-014-3069-3>.
- Balakrishnan A, Kanchinadham SBK, Kalyanaraman C. Respirometric assessment of vegetable tanning process wastewater generated from tanneries. *Eng Rep.* 2020;2:e12229. <https://doi.org/10.1002/eng.12229>.
- Vázquez G, Fernández-Agulló A, Gómez-Castro C, Freire MS, Antorrena G, González-Álvarez J. Response surface optimization of antioxidants extraction from chestnut (*Castanea sativa*) bur. *Ind Crops Prod.* 2012;35:126–34. <https://doi.org/10.1016/j.indcrop.2011.06.022>.
- Arbenz A, Avérous L. Chemical modification of tannins to elaborate aromatic biobased macromolecular architectures. *Green Chem.* 2015;17:2626–46. <https://doi.org/10.1039/C5GC00282F>.
- Das AK, Islam MN, Faruk MO, Ashaduzzaman M, Dungani R. Review on tannins: extraction processes, applications and possibilities. *S Afr J Bot.* 2020;135:58–70. <https://doi.org/10.1016/j.sajb.2020.08.008>.
- Vera M, Mella C, García Y, Jiménez VA, Urbano BF. Recent advances in tannin-containing food biopackaging. *Trends Food Sci Technol.* 2023;133:28–36. <https://doi.org/10.1016/j.tifs.2023.01.014>.
- Zhen L, Lange H, Crestini C. An analytical toolbox for fast and straightforward structural characterisation of commercially available tannins. *Molecules.* 2021;26:2352. <https://doi.org/10.3390/molecules26092352>.

33. Comandini P, Lerma-García MJ, Simó-Alfonso EF, Toschi TG. Tannin analysis of chestnut bark samples (*Castanea sativa* Mill.) by HPLC-DAD-MS. *Food Chem.* 2014;157:290–5. <https://doi.org/10.1016/j.foodchem.2014.02.003>.
34. Khatib M, Campo M, Bellumori M, Cecchi L, Vignolini P, Innocenti M, Mulinacci N. Tannins from different parts of the chestnut trunk (*Castanea Sativa* Mill.): a green and effective extraction method and their profiling by high-performance liquid chromatography-diode array detector-mass spectrometry. *ACS Food Sci Technol.* 2023;3:1903–12. <https://doi.org/10.1021/acscfoodscitech.3c00272>.
35. Grasel FDS, Ferrão MF, Wolf CR. Development of methodology for identification of the nature of the polyphenolic extracts by FTIR associated with multivariate analysis. *Spectrochim Acta A Mol Biomol Spectrosc.* 2016;153:94–101. <https://doi.org/10.1016/j.saa.2015.08.020>.
36. Venter PB, Sisa M, van der Merwe MJ, Bonnet SL, van der Westhuizen JH. Analysis of commercial proanthocyanidins. Part 1: The chemical composition of quebracho (*Schinopsis lorentzii* and *Schinopsis balansae*) heartwood extract. *Phytochemistry.* 2012;73:95–105. <https://doi.org/10.1016/j.phytochem.2011.10.006>.
37. Mattioli LB, Corazza I, Micucci M, Pallavicini M, Budriesi R. Tannins-based extracts: effects on gut chicken spontaneous contractility. *Molecules.* 2023;28:395. <https://doi.org/10.3390/molecules28010395>.
38. Noreljaleel AEM, Wilhelm A, Bonnet SL. Analysis of commercial proanthocyanidins. Part 6: sulfitation of flavan-3-Ols catechin and epicatechin, and procyanidin B-3. *Molecules.* 2020;25:4980. <https://doi.org/10.3390/molecules25214980>.
39. Panzella L, Napolitano A. Condensed tannins, a viable solution to meet the need for sustainable and effective multifunctionality in food packaging: structure, sources, and properties. *J Agric Food Chem.* 2022;70:751–8. <https://doi.org/10.1021/acs.jafc.1c07229>.
40. García DE, Glasser WG, Pizzi A, Paczkowski SP, Laborie MP. Modification of condensed tannins: from polyphenol chemistry to materials engineering. *New J Chem.* 2016;40:36–49. <https://doi.org/10.1039/C5NJ02131F>.
41. Ömür S, Mutlu MM. Modification of mimosa and quebracho tannins and the lightfastness properties of the processed leathers. *Tekstil Ve Konfeksiyon.* 2016;26(2):230–5.
42. Liu J, Ando R, Shimizu K, Hashida K, Makino R, Ohara S, Kondo R. Steroid 5 α -reductase inhibitory activity of condensed tannins from woody plants. *J Wood Sci.* 2008;54:68–75. <https://doi.org/10.1007/s10086-007-0905-9>.
43. El Gizawy HA, El Zanaty SA, El Ghaly EM, Seif-Eldein NA. Thevetia peruviana leaves, HPLC profile, isolation, and in vitro cytotoxicity. *RSC Adv.* 2023;13:12072–9. <https://doi.org/10.1039/d3ra00588g>.
44. Lugo L, Martín A, Diaz J, Pérez-Flórez A, Celis C. Implementation of modified acacia tannin by mannich reaction for removal of heavy metals (Cu, Cr and Hg). *Water.* 2020;12:352. <https://doi.org/10.3390/w12020352>.
45. Pizzi A, Stephanou A. A ¹³C NMR study of polyflavonoid tannin adhesive intermediates. I. Noncolloidal performance determining rearrangements. *J Appl Polym Sci.* 1994;51:2109–24. <https://doi.org/10.1002/app.1994.070511302>.
46. Zhao Y, Yan N, Feng MW. Biobased phenol formaldehyde resins derived from beetle-infested pine barks-structure and composition. *ACS Sustainable Chem Eng.* 2013;1:91–101. <https://doi.org/10.1021/sc3000459>.
47. Pizzi A, Stephanou A. A comparative ¹³C NMR study of polyflavonoid tannin extracts for phenolic polycondensates. *J Appl Polym Sci.* 1993;50:2105–13. <https://doi.org/10.1002/app.1993.070501209>.

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