

LOW CARBON PRODUCTS FOR THE DESIGN OF INNOVATIVE LEATHER PROCESSES. PART I: DETERMINATION OF THE OPTIMAL CHEMICAL MODIFICATION OF TARA

by

ANNA BACARDIT, CONCEPCIÓ CASAS, JORGE DÍAZ, ROSA CUADROS AND LLUÍS OLLÉ

A³ Chair in Leather Innovation. Igualada School of Engineering (EEI). Universitat Politècnica de Catalunya (UPC).

PLAÇA DEL REI, 15. 08700 – IGUALADA, SPAIN

ABSTRACT

This study considers the fruit of the tara bush as a sustainable source of tanning agents and proposes alternatives to the mineral salts and vegetable extracts for commercial use. Specifically, in part I of the study various processes of physical and chemical modification were developed in order to obtain a modified tara with a higher percentage of tannins which can therefore improve their tanning capability. Several aqueous extraction processes at different temperatures were developed and optimized in order to decrease the astringency and facilitate the penetration of the tannin molecules through the leather structure.

RESUMEN

Este estudio considera el fruto del arbusto tara como fuente sostenible de agentes curtientes y propone alternativas a las sales minerales y extractos vegetales para uso comercial. Específicamente, en la parte I del estudio diversos procesos de modificación física y química se han desarrollado con el fin de obtener una tara modificada con un mayor porcentaje de taninos que permita mejorar su capacidad de curtido. Varios procesos de extracción acuosa a diferentes temperaturas se han desarrollado y optimizado con el fin de disminuir la astringencia y facilitar la penetración de las moléculas de tanino a través de la estructura de cuero.

INTRODUCTION

Tara tanning agents are well known in the leather industry and are highly appreciated because of their light color and light fastness. For this reason, the demand of tara tannins has increased over the last few decades, as has the production of leather for automobile upholstery¹. Tara powder is a hydrolysable tannin formed by a core of sugar molecules such as glucose, coupled with phenolic carboxylic acids, for instance gallic acid and its derivatives. The ester linkages are formed between the alcohol groups (-OH) of the sugar molecule and the carboxylic groups (-COOH) of the molecules of phenol-carboxylic acids. The number of ester linkages in a molecule of tannin depends on the sugar molecules present at the core of the tannin molecule. Their properties can be summarized as:

- Low stability to hydrolysis and microorganisms: hydrolysis of the ester bonds by acids and enzymes (esterase) causes the loss of tannin.
- High acidity: tara solutions have a pH of 3.0 - 3.5 due to high concentration of acids.
- Slow penetration into the skin structure.
- Light fastness.
- High salt concentration buffers: these are salts of weak organic acids, which provide good protection to the leather against ageing and acid hydrolysis.

Tara powder is highly appreciated by the leather industry as a source of vegetable tannins, which allow light colors to be obtained; the leather articles produced are full, soft, with a firm and smooth grain and with good light fastness. Tara is easily soluble in water and does not contain color substances as it occurs with other vegetable tannins. Tara powder can be used to tan all kind of hides and skins and to re-tan chrome tanned leathers to improve grain tightening. The main



Figure 1. Molecular Structure of Gallotannic Acid.

application is in the manufacture of leather for car seats. The general specifications for commercially available tara powder for tanning applications are as follows: minimum of 48% of tannin content, maximum of 13% of water content, and pH (at 6.9°Bè) of 3 - 4.

However, tara tannins have some disadvantages when compared to other vegetable tannin extracts:

- High concentration of insoluble solids (if tannins are not extracted properly, tara powder retains high amounts of cellulosic compounds from the tara pods).
- Tanning limits when tara tannin is the single compound for tanning are reduced. The hydrolyzation of vegetable tannins cannot increase the shrinking temperature.
- Readily production of complexes with iron and other metals and formation of dark spots on the leather. Tara mills and several machines used in the mechanical operations of leather processing usually contain iron parts, which increases the risk of obtaining such dark spots.

To obtain tara extract, the tara powder has to be treated at 65-70°C for 30-40 minutes, water with 4 to 5 parts of the weight of the powder is added, and the liquor is washed 5 times. Then the liquor is purified by decantation and filtration, and concentrated from 2-5° Bè to 11-12°Bè. The powder of tara tannin extract is obtained by atomization. Tara extract is used to obtain tannic acid, and it has valuable applications in the food and beverage industries: it is used to clarify and give astringency to wine, tea, coffee, cocoa, beer and other food. Recent investigations demonstrate that tara tannin and its derivatives have excellent properties as antioxidant agents to prevent cardiovascular diseases. Also, these tannins have astringent properties of pharmaceutical applications that prevent irritation by reducing protein coagulation. The tannic acid is used as a hemostatic to cut down hemorrhages and, mostly, for treating burns²⁻⁷.

MATERIALS AND METHODS

This study was conducted in three stages:

1st stage. Several samples of the original tara powder were analysed to find out about the concentration of tannin by the filter method.

2nd stage. Development of several physical-chemical extraction processes from commercially available tara as provided by Leather Quimica in order to obtain a tara extract with high tannin contents and low insoluble matter.

3rd stage. Optimization of the tannin extraction process and application to the leather.

Analytical Characterization of Tara

Several samples of the original tara powder were analyzed to learn about the concentration of tannin following the filter method. To determine the quality of the vegetable tannins, the following parameters are examined:

- Tannin content by the filter method.
- Non-tannin content by the gravimetric method.
- Insoluble matter by the gravimetric method.
- Total solids by the gravimetric method.
- Soluble solids by the gravimetric method.
- Iron content by the atomic absorption spectroscopy (AAS) method.

Extraction Processes of Tara

Three different extraction processes were carried out:

Aqueous extraction at different temperatures. To perform this thermal process, solutions of tara at 10% content were prepared and treated at 70°C and 136°C by autoclave for 6 and 3 hours, respectively. After that, the solutions were filtered using a fabric filter and finally the content of tannins was determined.

Chemical extraction using acid and alkali. To carry out this chemical extraction, 2 solutions were prepared, the first one using 20 g of tara, 200 mL of water and 0.5 mL of 50% NaOH (basic process). The second one was prepared using 20 g of tara, 200 mL of water and 0.5 mL of 33% HCl acid process). Each process was treated at 70°C and 136°C by autoclave for 6 and 3 hours, respectively. After that, the solutions were filtered by means of a fabric filter and finally the content of tannins was determined.

Chemical modification process by sulphitation. To perform this chemical extraction, 3 solutions were prepared, the first one using 10 g of tara, 100 mL of water, 1 mL of 50% NaOH and 1 g of sodium metabisulphite. The second one was prepared using 10 g of tara, 100 mL of water, 1 mL of 33% HCl and 1 g of sodium metabisulphite. The third one was prepared using 20 g of tara, 200 mL of water and 1 g of sodium metabisulphite. Each process was treated at 70°C and 136°C by autoclave for 6 and 3 hours, respectively. After that, the solutions were filtered using a fabric filter and finally the tannin content was determined.

Optimization of the Tannin Extraction Process

In order to optimize the extraction process, a thermal extraction process was carried out. In this process, 10% tara solutions were prepared and treated at 40°C and 70°C for 6 and 3 hours, respectively. Next, the solutions were filtered with fabric and the tannin content was determined.

Tara tannins are notable for their high acidity and on mild acid hydrolysis. The tannin gives gallic acid, and instead of the usual carbohydrate fragment, it gives the alicyclic quinic acid⁵. The acidity of the tannin is directly related to the presence of the free carboxyl group of quinic acid in its structure. Free

TABLE I
Acid and alkali treatment of tara powder.

	I	II	III	IV	V	VI	VII	VIII
Commercially available Tara (g)	2	2	2	2	2	2	2	2
H ₂ O (mL)	20	20	20	20	20	20	20	20
HCL 33% (mL)	0.1		0.05	0.05				
NaOH 50% (mL)		0.1			0.05	0.05		
Temperature (°C)	70	70	70	136	70	136	70	136
Time (h)	6	6	6	3	6	3	6	3

TABLE II
Pre-tanning formulation.

STAGE	°C	%	PRODUCT	Gr.	Time
Pre-tanning	20				
		84	Tara Extract 40°C / 70°C		
		7	Synthetic S-3		
		2	Sulphite oil	Aut. night	Cross section testing
		0.8	Formic acid	2h	pH=3.59
					Drain
Washing	20	300	Water	20'	Drain
					Rest on horse
					Samming
					Drying

gallic acid and other organic acids present in the powder are non-tannin compounds, as well as carbohydrates. For this reason, the solutions shown in Table 1 of modified tara were analyzed by HPLC to determine the gallic acid content. This will give an idea of the hydrolysis of the tara tannins and whether this determination can be used to test the quality of the tara products.

Finally, the solutions of aqueous extractions resulting from the optimization process at low temperature were applied to leather samples. The application of modified Tara in the pre-tanning process was studied. The aim was to reduce the amount of synthetic pre-tanning agents.

The products of the experimental test were: tara extracted at 40°C and 70°C during a time process of 6 hours. Bovine pickled hides (pH 3.5) were used to perform the experiment. The formulation of pre-tanning process is shown in Table 2.

RESULTS AND DISCUSSION

Analytical Characterization of Tara

Table III shows the results of the analysis of the different tara samples.

As can be observed, there is variability between different samples. The tannin content ranges between 45% and 50%. The concentration of insoluble matter, which is a negative factor for tanning process with tara due to the large amount of insoluble material remaining in the wastewater, also presents a significant variability. Concerning iron content, no significant differences were found between the samples observed except for sample 3 which has a remarkably high iron content.

Extraction Processes of Tara

Three types of extraction processes were carried out to obtain a tara extract with high tannin content and low content of insoluble matter.

Extraction at Different Temperatures

Table 4 shows the results of the analysis of the tara solutions concentrated at 9% of water approximately after the thermal processes of extraction.

It can be observed how the tara powder obtained has higher tannin content and a content of insoluble matter almost negligible when compared with the commercially available tara powder.

As for the aqueous extraction process, a slightly better result was obtained at 136°C, although the difference with the process at 70°C is negligible, since the extracts obtained were with 62% and 61% of tara, respectively.

Chemical Extraction Using Acid and Alkali

Table 5 shows the results of the analysis of the solutions of tara concentrated at 9% of water approximately after the acid and alkali processes of extraction.

The concentration of tannins increases considerably and the insoluble fraction shown is fairly limited. The process at 70°C shows better results than at 136°C because of the increase in proportion of non-tannin due to tannin hydrolysis itself. The chemical extraction process results in greater concentration of tannins for the extracts obtained at 70°C. As can be seen in the results, no observable differences of basic or acid conditions have been obtained. At 136°C, the fraction of non-tannins increases significantly, evidencing the hydrolysis process of the tannins. Extracts are obtained with high tannin content and very low concentration of insoluble matter.

TABLE III
Characterization of commercially available samples of tara powder.

Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Average
Soluble Solids (%)	58.9	67.9	59.7	60.1	61.6
Total Solids (%)	85.9	92.2	92.9	84.8	88.9
Non-Tannins (%)	12.0	17.9	14.7	13.7	14.6
Tannins (%)	46.9	50.1	45.0	46.5	47.1
Insoluble Matter (%)	27.0	24.2	33.2	24.6	27.2
Water (%)	14.1	7.8	7.1	15.2	11.0
Iron (mg/Kg)	182.0	204.0	388.9	159.0	233.5

TABLE IV
Tannin content of tara after thermal extraction.

Determination	70°C	136°C	Initial Tara powder
Soluble Solids (%)	84.0	88.0	59.7
Total Solids (%)	91.0	91.0	92.9
Non-Tannins (%)	24.5	26.0	14.7
Tannins (%)	61.25	62.1	45.0
Insoluble Matter (%)	7.0	2.9	33.2

Chemical Modification Process by Sulphitation

Table 6 shows the results of the analysis of the tara solutions concentrated at 9% of water approximately after the sulphitation processes of extraction.

A modified tara with high concentration of tannins was obtained. It was observed that the best process is developed in the presence of metabisulphite. The addition of base and/or acid is a negative factor because it leads to the conditions for the chemical hydrolysis of tannins. We can observe an increase in non-tannin fraction and a decrease in tannin containing fraction. Also, the process is much more satisfactory at 70°C than it is at 136°C since there is an increase in non-tannic fraction. Therefore, this process was rejected due to the increase of percentage of non-tannins.

Optimization of the Tannin Extraction Process

Thermal extraction process

The extraction processes tested were divided into aqueous processes and chemical processes. As has been observed, the best results are obtained in the aqueous process since the addition of acids or bases to the extraction solution contributes to the processes of hydrolysis and tannins are hydrolyzed, thus increasing the fraction of non-tannins. As regards thermal processes, no significant differences are observed between extraction at 70°C and at 136°C. A tara extract with a tannin concentration of 62% was obtained. Taking into account that the initial tara had an average concentration of tannins of 47%, the increase in tannic fraction is considerable.

It should also be noted that another objective of these processes of extraction was to obtain a decrease in insoluble matter fraction. The objective was achieved since that fraction was 33% in the initial commercially available and was reduced to 1-7% in the extracts. In order to optimize the process, aqueous extractions of tara were carried out at lower temperatures. By doing so, the energy costs of the process were reduced. Table 7 shows the results of the analysis of the

solutions of tara concentrated at 9% of water approximately after the aqueous processes of extraction.

It can be noticed that the temperature factor does not significant to obtaining a greater percentage of tannins. However, a higher content of tannins can be obtained with a longer extraction process.

Application of Optimal Modified Tara

Shrinkage temperature was determined to evaluate the thermal stability of leathers obtained with the application of modified tara. The results are shown in Table VIII.

As can be observed, the penetration of the extract into the leather cross section is poor and the shrinkage temperature is low, lower than that of the original powder. Leather appearance is slightly worse; there is more shrunk grain shrinking and astringency, and penetration is not sufficient.

TABLE V
Tannin content of tara after acid and alkali extraction processes.

Determination	Acid process		Basic process		Initial Tara powder
	70°C	136°C	70°C	136°C	
Soluble Solids (%)	86.2	88.2	86.2	86.8	59.7
Total Solids (%)	91.0	91.0	91.0	91.0	92.9
Non-Tannins (%)	25.5	30.8	25.5	30.8	14.7
Tannins (%)	60.6	57.4	60.6	57.4	45.0
Insoluble Matter (%)	4.7	2.8	4.7	2.8	33.2

TABLE VI
Tannin content of tara after sulphitation processes.

	I		III		V		Initial Tara powder
	70°C	136°C	70°C	136°C	70°C	136°C	
Soluble Solids (%)	81.1	91.0	85.2	87.2	91.0	87.2	59.7
Total Solids (%)	91.0	92.0	91.0	91.0	91.0	91.0	92.9
Non-Tannins (%)	29.8	56.4	37.6	43.6	27.8	34.1	14.7
Tannins (%)	52.9	36.4	47.7	42.3	63.2	53.1	45.0
Insoluble Matter (%)	8.3	1.0	5.8	3.8	1.0	3.8	33.2

TABLE VII
Tannin content of tara
after aqueous extraction.

Determination	40°C/3h	40°C/6h	70°C/3h	70°C/6h
Soluble Solids (%)	89.2	84.9	91.0	89.3
Total Solids (%)	91	91	91	91
Non-Tannins (%)	22.7	19.7	22.7	20.2
Tannins (%)	66.5	71.3	68.2	67.4
Insoluble Matter (%)	1.7	6.1	0.0	1.7




CONCLUSIONS

The extraction processes tested were grouped into physical processes and physical and chemical processes. The best results are obtained with the physical processes (thermal processes) since the addition of acids or bases to the extraction solution favor hydrolysis processes and tannins are hydrolyzed, the fraction of non-tannins is therefore increased. This occurs because the tara tannins are hydrolysable tannins, polyphenolic compounds formed by a carbohydrate (glucose) combined with several molecules of polyphenols, with gallic acid as its monomer. In the hydrolysis process, gallic acid monomers are released causing the increase in non-tannin fraction.

As for thermal processes no significant differences were observed between extraction at 70 °C and at 136 °C. The tara extract obtained had a tannin concentration of 62%. Considering that the initial tara had a tannin concentration of 45%, the increase in tannic fraction is significant. A further objective of the study was to obtain a reduction of insoluble matter fraction through the applied extraction process. This objective was achieved, since this fraction was reduced from 33% content in the initial commercial Tara powder to 1-7% in the tara aqueous extracts. In order to optimize the process, aqueous extraction tests were carried out at lower temperatures, which in itself is an advantage since it is energy-saving.

Regarding the use of modified tara (optimized aqueous extracts) in the pre-tanning process, the results obtained were slightly worse than when applying the tara powder directly. Considering this, it is necessary to broaden and deepen the study to improve the properties of the modified tara with respect to the size of the particle.

TABLE VIII
Shrinkage temperature
and leather cross section.

Sample	Ts (°C)	Cross section
Aqueous tara extract 40°C/6h	56	
Aqueous tara extract 70°C/6h	58	
Original tara powder	61	

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