Qualitative aspects of sheep hides tanned with Black Jurema and Red Angico

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Abstract

Vegetable tannins, used by the tanning industry, are considered to be eco-friendly because of their natural tanning agents. They are composed of polyphenols and are divided into hydrolysable and condensed tannins. Hydrolysable tannins are glucose polyesters classified into gallic or ellagic tannins. Condensed tannins, however, consist of catechin monomers, known as flavonoids. The native sources of plant extracts for tanning hides, the tanning potential of the barks of Black Jurema (*Mimosa tenuiflora* [Willd.] Poir.) and Red Angico (*Anadenanthera macrocarpa* [Benth.] Brenan.) trees were evaluated; these species were collected from the semi-arid region of Morada Nova, in the state of Ceará, and from the *cerrado* biome region of Campo Grande, state of Mato Grosso do Sul (Brazil), respectively. These extracts were characterized and classified as condensed tannins. When compared to the black wattle (*Acacia mearnsii* De Wild), these tannins presented a lower extraction yield as well as lower light fastness. The tanning methodology used in the Morada Nova sheep hides was the same as that used in the evaluation of black wattle. The leather was not re-tanned or greased, and no auxiliary products were used in the tanning process. The tensile strength (ABNT NBR ISO 3376:2014) of the leather tanned with Jurema does not differ significantly ($P>0.05$) from the leather tanned with Angico. The leather tanned with Angico showed higher tear strength ($P<0.05$) in the tests performed according to the procedures defined in the ABNT NBR ISO 3377-1 (2014) and 3377-2 (2014) guidelines. It also presented higher shrink resistance (ABNT NBR 13335:2001).

Key words: Black Jurema, Red Angico, Vegetable tannins

1 - Introduction

The increasingly stricter tanning regulations, which also require the recycling of tannery residues, have compelled the tanning industry to produce leather without the use of chromium (Plavan et al. 2009). Developing technologies that are less harmful to the environment involves the combination of organic/inorganic chromium-free materials, also known as eco-friendly products. (Covington and Lampard 2004; Saravanabhavan et al. 2004).

Among the organic materials used as tanning agents, it is important to emphasize the role of vegetable tannins. Vegetable tanning extracts are complex mixtures of several substances, among them the phenolic extracts with tanning power. Accumulated in certain tissues, tannins are commonly found in wood (core), bark, roots, leaves, fruit and seeds. According to their hydrolysis behavior, they can be classified as hydrolysable tannins and condensed tannins (Hoinacki 1989). Hydrolysable tannins are glucose polyesters and can be classified as gallic tannins or ellagitannins, depending on the acid formed during their hydrolysis (Pizzi 1993). On the other hand, condensed tannins are constituted of catechin monomers and are known as flavonoids (Haslam 1966; Wenzl 1970; Pizzi 1993).

Some types of tannins can be extracted from the bark of trees using simple industrial processes as they are soluble in water (Latif 1966). According to Hergert (1962), tannins can reach from 2 to 40% tannin from the dry matter of the barks of several species. The tannin concentrations vary considerably according to species, age and part of the vegetable. Moreover, depending on the tanning source used, the tannins extracted yield different organoleptic and chemical properties to the leather produced (Covington 2006). Thus, further studies are necessary on alternative tannin sources so they can be industrially used in the manufacturing of economically feasible leather, with desirable market characteristics.

In light of the great vegetation diversity in Brazil which contains tanning substances and due to the increasing demand for tanning products with low environmental pollution potential (eco-friendly), this study assesses the tanning potential of the barks of Black Jurema (*Mimosa tenuiflora* [Willd.] Poir.) and Red Angico (*Anadenanthera macrocarpa* [Benth.] Brenan), both species found in the native vegetation of the Brazilian *cerrado* and semi-arid regions.

2 - Material and Methods

2.1 - Collection and grinding of the studied tannins

The barks from both vegetable species under study were collected from two different regions in Brazil. The barks from Black Jurema (*Mimosa tenuiflora* [Willd.] Poir.) were collected in the semi-arid tropical region in the city of Morada Nova, in the State of Ceará, and those from Red Angico (*Anadenanthera macrocarpa* [Benth.] Brenan.) in the *cerrado* region of the city of Campo Grande, in the State of Mato Grosso do Sul.

Fresh barks from Black Jurema and Red Angico were oven dried with air circulation at 55 ± 5°C for 72 hours. After drying, the samples were ground in a Retch ZM 200 ultracentrifuge mill at 8000 rpm, equipped with a 0.75-mm sieve in order to obtain a very thin particulate and homogeneous material. After fragmentation, the ground material was stored in plastic bags.

2.2 **-** Chemical characterization of the tannin ground barks

The extracts were compared with reference standards prepared with an aqueous solution consisting of 0.1 mg/mL tannic acid; aqueous solution of 0.1 mg/mL gallic acid and 0.1 mg/mL catechin in methanol.

Five chemical tests were performed to characterize the tannin type (Falcão and Araújo 2011). The analyses were performed in triplicates with the dry and ground bark samples from Black Jurema and Red Angico.

<u>Ferric assay</u>

The ferric assay is used in to determine tannins in general. Ferric chloride reacts with phenols forming a dark blue or dark green color. The blue coloring indicates the presence of hydrolysable tannins and the dark blue color indicates condensed tannins. For the assay, 1 mg of the sample hydrated in 2-mL water was used, with the addition of 2 drops of 2% ferric chloride (w/v) to the sample, observing the color formed.

Vanillin assay

This assay is used for the determination of condensed tannins. Vanillin, in acid conditions, reacts with flavonoids, yielding a red product. This is a very sensitive analysis and is not sufficient for determining condensed tannins. Confirmation is then necessary with the acid butanol assay. The test was performed using 1 mg of the sample, with the addition of 2 drops 1% vanillin (w/v). The mixture was then homogenized and 2 drops of HCl p.a were added. The formation of a red color indicates the presence of condensed tannins.

Acid butanol assay

The acid butanol assay promotes the oxidation of condensed tannins, resulting in a reddish color. This assay, together with the vanillin assay, is efficient for determining condensed tannins. For such, 5 mg of the sample was used, adding 2.4 mL acid butanol and 1 drop of 2% ammonium ferric sulfate (w/v). This mixture was then heated at 100°C for 50 minutes. The formation of an orange-reddish or red color indicates the presence of condensed tannins.

Nitrous acid assay

Ellagitannins react with nitrous acid forming a green color. Nitrous acid is obtained through the dissolution of sodium nitrite in HCl. The assay was performed on 5 mg of the sample and adding 2 mL pyridine. Then, 3 drops of HCl p.a were added and the sample was homogenized and heated at 30 °C for 5 minutes. After heating, 3 drops of 1% sodium nitrate (w/v) were added, and the mixture was homogenized and incubated for 20 minutes at 30°C. The formation of a green color indicates the presence of ellagitannins.

Rhodamine assay

In a basic solution, rhodamine reacts with the hydroxyl groups free of gallotannins, forming a pink complex. In order to be considered gallotannin, the sample cannot be positive for ellagitannins or condensed tannins. this assay was performed using 1 mg of the sample, adding 2 drops of rhodamine. After 5 minutes, 2 drops of KOH 0.5N were added. There was a 5 minutes waiting period. The formation of a pink color indicates the presence of gallotannins.

2.3 - Extraction and chemical characterization of tannin extracts

The extractions of tannic substances were performed with the dry ground bark in aqueous solution heated to boiling in reflux for 2.5 hours, and the temperature kept by means of a heating blanket. The chemical characterization of the extracts was assessed by its tanning content, astringency and gravimetric yield. The analyses were performed in duplicates. The tannin extracts under study were compared with the tannin extract from Black Wattle (*Acacia mearnsii* De Wild) commercially available and used in tanneries.

2.4 - Processing of sheep hides

This study used eight Morada Nova male sheeps, raised at Embrapa Pecuária Sudeste (21°57'31.0"S 47°50'34.9"W) and slaughtered at approximately 9 months old. The hides were shaved with sodium sulfite (3%), lime (3.5%), surfactant (0.5%) and water (12 to 15%), using kaolin to adjust Baume at 28°. The paste was spread over the fleshy part and after 5 hours the fur was removed using a polymer spatula. All skin mass percentages were calculated. The unhairing process was performed in dye drums using water (200%), surfactant (0.5%) and lime (1.0%), for 12 hours. Following this procedure, deliming was performed with non-swelling organic acids (1.5%) to remove the alkaline substances deposited or chemically combined with the collagen from the hide, used in the previous step. In the purging stage, a protolithic enzyme (0.03%) and surfactant (0.5%) were used for 60 minutes. In the pickling phase, water (80%), sodium chloride (8%) and formic acid were used to pH stabilization of 3.2. In the tanning process, three additions of 20% tannin sample (considering the weight of the pickled hide + 40%) were performed, and the process lasted for 24 hours. In this study, four hides were tanned with Black Jurema and four with Red Angico without using auxiliaries for tanning, re-tanning and finishing. Next, the leather was left to dry in a shaded area and then sanded.

After tanning, electron-micrographs of the surface and cross section of the leather were performed using a Field Emission Gun-Scanning Electron Microscopy (FEG-SEM) Philips XL 30.

2.5 - Leather qualitative assessment

The qualitative aspects of leather were assessed using tensile strength and tear resistance tests, as well as color fastness, aging by heat and retraction temperature tests. A completely randomized experimental design was used in the analysis of the results, where each animal represented a parcel, the effects of direction of the sub-parcels and the test samples of the sub-sub-parcels. Data were analyzed using the Tukey test with 5% probability, using a GLM (General Linear Model) procedure of SAS (2003).

Physical-mechanical assays

The determinations of tensile strength, elongation and tear resistance were performed using the methodologies defined in standards ABNT NBR ISO 3376 (2014), ABNT NBR ISO 3377-1 (2014) and ABNT NBR ISO 3377-2 (2014). The test samples were conditioned according to the methodology defined in standard ABNT NBR 10455 (2014).

Color fastness, heat aging, and retraction temperature tests.

The determinations of color fastness, heat aging and retraction temperature were performed according to the methodologies defined in standards ABNT NBR ISO 105-B02 (2007), ABNT NBR 15170 (2013) and ABNT NBR 13335 (2001).

3 - Results and Discussion

3.1 - Chemical characterization of the ground barks and tannin extracts

Table 1 shows the results of the chemical tests for the characterization of tannins in the barks of the two species. The following colors were observed in the ferric, vanillin and acid butanol assays: green, red and reddish, respectively, indicating the presence of condensed tannins. No green coloring was observed in the nitrous acid assay, thus indicating the absence of ellagitannins. In the rhodamine test the Black Jurema and Red Angico tannins presented negative results for gallotannins, given the similarities found in the literature, since according to Falcão and Araújo (2011) they were classified as condensed tannins.

Table 1. Chemical test results for the tannins.

Species	Assays				
	Ferric	Vanillin	Acid butanol	Nitric Acid	Rhodamine
Angico	+ C	+ C	+ C	- E	- G*
Jurema	+ C	+ C	+ C	- E	- G

Legend: C= condensed tannins; E = Ellagitannins; G = Gallotannins; + = presence; - = Absence.
* Lightly pink.

Table 2 shows the median and standard error results for the analyses, performed in triplicates, for the chemical characterization of ground barks. The tanning content of the Black Jurema bark was higher than that of Red Angico. The highest (dark) color parameter of Red Angico can be a limiting factor for its usage, since it influences the final color of the leather and hinders the dye process with light colors.

Some authors (Trugillho et al. 1997) assessed the percentage of tanning agents in Red Angico (18.51%) and also in other nine vegetable species in the *cerrado* region of Minas Gerais and found the percentages of condensed tannins in barks ranging from 1.3% (*Platycyamus regnellii*) to 18.6% (*Piptadenia gonoacantha*), using well-known sources of tannins, such as *Peltophorum dubium* (10.6%).

Paes et al. (2006a) assessed the tanning potential and tanning capacity of the following forestry species found in the Brazilian semi-arid: Red Angico, Cashew, Black Jurema, Red Jurema, Algarroba and

Quince. From these species, Cashew, Red Jurema and Black Jurema presented, respectively, 19.8%, 18.1% and 17.7% tannins on their bark. Angico presented 11.9%, lower ($P<0.05$) than the three species mentioned. Algarroba and Quince presented 3.0% and 6.6%, respectively.

Table 2. Result means from the analyses of ground bark chemical characterization for the two species.

Parameter	Mean ± Standard Error (n=3)	
	Black Jurema	Red Angico
Tanning (%)	26.5±0.5	22.2±0.6
Not tanning (%)	13.5±0.3	5.9±0.1
Insoluble (%)	52.9±0.6	61.3±0.7
Humidity (%)	7.1±0.0	10.6±0.0
Total solid (%)	92.9±0.0	89.4±0.0
Tanning (%) (H=6%)	26.8±0.5	23.3±0.6
Astringency (T/Nt)	2.0±0.1	3.7±0.0
Color (v/a)	0.7/1.6	5.7/9.5
Ashes (% b.s.)	3.2	5.8
Iron (%)	0.02	0.02
pH (solution at 10% v/v)	4.5	5.5
Tannin type	Condensed	Condensed

Legend: H = air relative humidity, n= number of replicates.

Paes et al. (2010) analyzed the concentration of tannins in the bark, trunk (core) and roots, fruit (with and without seeds), leaves, flowers and branches of Red Angico and found 13.95% tannins in the bark. The values found by Paes et al. (2006a and 2010) were lower than the values found in this study for the tannin content in the bark of Red Angico (23.3%) and Black Jurema (26.8%).

The Red Angico bark is considered a high-astringency material (3.7) and the bark from Black Jurema is considered as moderate astringency (2.0) (Table 2). Very astringent materials can cause over tanning, overloading the external layers of the hides, however do not penetrate and adequately tan the internal layers, resulting in a hard and wrinkled surface layer. According to Hoinacki (1989), a moderately astringent material has a value ranging from 2 to 3. In low astringency materials, the tannin/non-tanning ratio is 1. The leather tanned with Angico bark, since it has a high astringency value, resulted in a coarse and rough to the touch leather. The opposite happened with the leather tanned with Jurema.

In the chemical characterization of Red Angico extract (62.7%), a higher percentage of tannin agents was found when compared with the extract from Black Jurema (53.7%) (Table 3), as opposed to what was found in the barks. However, the percentage of tanning agents on the tannins studied is lower than the percentage of tannins from the Black Wattle extract.

Table 3. Average values in the chemical analyses of tannin extracts.

Parameters assessed	Black Jurema	Red Angico	Black Wattle
Tanning (%) (H=6%)	53.7	62.7	72.0
Astringency (T/Nt)	2.0	3.0	4.0
Gravimetric yield (% b.s.)	3.3	4.1	2.5

Legend: H= air relative humidity, n= number of replicates.

Trugillho et al. (1997) found percentages of condensed tannins in the extract ranging from 12.8% in Jacaranda Mineiro (*Jacaranda cuspidifolia*), to 35.5% in Red Angico. Red Angico and Açoita Cavalo (*Luehea divaricata*) were the species with the highest content of extracts soluble in hot water, with 35.5 and 33.7%, respectively, while the species presenting the lowest content were Angico Cangalha (13.9%) and Jacaranda Mineiro (12.8%). According to the authors, the percentage of tanning agents found in the Red Angico extract was lower than the percentage found in this study (62.7%).

Black Jurema and Red Angico are considered tannins of moderate astringency, with respective values of 2.0 and 3.0 (Table 3). The astringency of the tannins under study is lower than the astringency of Black Wattle (4.0). Since the percentage of tanning agents and astringency value of Black Jurema extract are lower than the values from the extracts commonly used for tanning hides, this extract could be used in a pre-tanning stage.

The gravimetric yield is related to the amount (kg) of dry barks needed to obtain 1 kg of pure tannin. Black Jurema had the lowest gravimetric yield (3.3%) when compared to Red Angico (4.1%). Therefore, less Black Jurema bark is necessary to obtain 1 kg of the product. For tanning with a lower amount of the sample, the tannin extraction process is necessary for Black Jurema and for Red Angico, since the tanning content of the extract is much higher than that of the bark, and the astringency values of the extracts are also lower, thereby resulting in greater tanning efficiency.

3.2 - Processing of sheep hides

The leather tanned with the bark of both tannins presented smooth surface layers (Figures 1A and 1B), similar to the tanning with Black Wattle, a commercial tannin commonly used in tanneries. As observed in the transversal cut, the filling of leather tanned with Black Jurema bark (Figures 1C and 1E) was lower than that for Red Angico (Figures 1D and 1F). The tanning with Red Angico tannin made the collagen fiber bundles more voluminous than the fiber bundles from Black Jurema. The filling is a characteristic of the type of tanning agent, since the subtracts (sheep hide) are similar, the animals are of the same breed (Morada Nova), same gender (male) and similar ages (9 months).

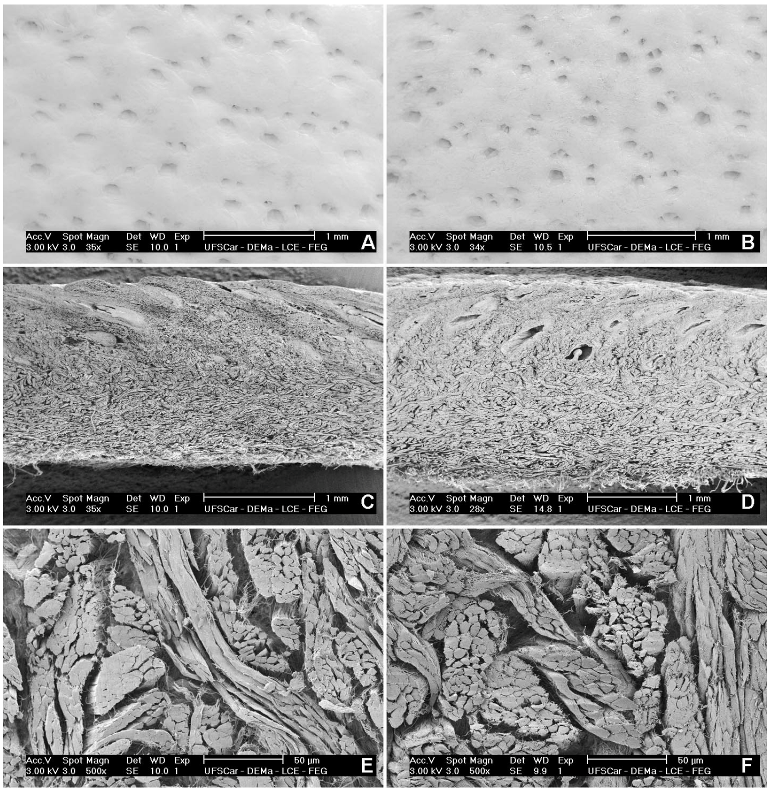

Figure 1. The images were produced using a Field Emission Gun-Scanning Electron Microscopy (FEG-SEM). Leather surface and cross section of leather tanned with Black Jurema (A, C, E); Leather surface and cross-section of leather tanned with Red Angico (B, D, F). Magnification: images A, B, C and D = 35x, images E and F = 500x.

3.3 - Leather qualitative assessment

<u>Physical-mechanical assays</u>

The thickness of leather for the physical-mechanical assays are significantly different ($P<0.05$) in both tannins studied (Table 4). The leather tanned with Red Angico was thicker when compared with the leather tanned with Black Jurema, thus confirming the greater leather thickness observed in Figures D1 and F1.

The tensile strength did not differ significantly (P>0.05) either in relation to the tannins used in the tanning or in relation to the removal direction of the sample.

Table 4. Results of tensile strength and elongation percentage according to ABNT NBR ISO 3376 (2014).

Species	Determination of tensile strength and percentage extension					
	Thickness (mm)		Resistance (N/mm^2)		Elongation (%)	
	L	T	L	T	L	T
Red Angico	2.70^{Ab}	3.03^{Aa}	14.52^{Aa}	14.23^{Aa}	31.76^{Ab}	43.76^{Aa}
Black Jurema	2.07^{Ba}	2.05^{Ba}	16.14^{Aa}	14.91^{Aa}	28.70^{Ab}	36.97^{Aa}

Legend: Means followed by different capital letters, vertically, or small-case letters, horizontally, for each parameter analyzed, indicate significant differences (P<0.05) by Tukey's test.
L= longitudinal direction, parallel to the backline; T= transversal to the backline

Lima et al. (2014) found higher tensile strength and elongation values for leather tanned with Black Jurema tannins in both directions than those for leather tanned with Red Angico tannin. However, Paes et al. (2006b) found that leather tanned with Black Jurema tannin had higher tensile strength in the longitudinal direction than the leather tanned with Red Angico. However, in the transversal direction, as in this study, they found no significant differences in relation to the leather tanned with Red Angico and Black Jurema. The tensile strength results of leather found by both authors were higher than the ones found in this study, since the leathers they used were re-tanned.

As for elongation (Table 4), the leather tanned with Angico and the one tanned with Jurema, in both directions, the results are significantly different (P<0.05) with higher values for transversal direction (T).

The thickness of the leather tanned with Red Angico were always greater than the leather tanned with Black Jurema tannin (P<0.05) (Table 5). The direction did not affect the thickness of the leather, except for the thickness of the leather tanned with Red Angico tanning, since it was higher in the transversal direction (P<0.05).

Table 5. Results of the tear strength tests on simple edges, according to standard ABNT NBR ISO 3377-1 (2014) and double edges according to standard ABNT NBR ISO 3377-2 (2014).

Species	Result of tear strength simple edge				Result of tear strength double edge			
	Thickness (mm)		Force (N)		Thickness (mm)		Force (N)	
	L	T	L	T	L	T	L	T
Red Angico	3.04^{Ab}	3.38^{Aa}	36.07^{Aa}	37.59^{Aa}	2.77^{Aa}	2.78^{Aa}	82.16^{Aa}	77.82^{Aa}
Black Jurema	2.29^{Ba}	2.18^{Ba}	26.71^{Ba}	23.61^{Ba}	2.08^{Ba}	2.22^{Ba}	60.66^{Ba}	64.66^{Ba}

Legend: Means followed by different capital letters, vertically, or small-case letters, horizontally, for each parameter analyzed, indicate significant differences (P<0.05) by Tukey's test.
L= longitudinal direction, parallel to the backline; T= transversal to the backline

The leather tanned with Red Angico had greater tear resistance (ABNT NBR ISO 3377-1:2014 and ABNT NBR ISO 3377-2:2014) than those tanned with Black Jurema in both directions. The same results were observed by Paes et al. (2006b). However, Lima et al. (2014) observed the opposite, the leather tanned with Black Jurema had greater tear resistance than those tanned with Red Angico. The direction of the samples did not affect the tear strength values (P>0.05) (Table 5).

Color fastness, heat aging, and retraction temperature tests
In the heat aging test, the shrinking of the leather tanned by both tanning species was evident (Table 6). The leather tanned with Red Angico reached, with aging, grade 3 in the gray scale and the leather tanned with Black Jurema reached grade 2, that is, the leather tanned with Black Jurema has a greater potential for color fading than the leather tanned with Red Angico.

Table 6. Results of heat aging and color fastness tests for leather tanned with the studied tannins.

Species	Heat aging	Color fastness
Red Angico	Grade 3 in the gray scale	Grade 1 in the blue scale
Black Jurema	Grade 2 in the gray scale	Grade 1 in the blue scale

In the color fastness assay, the leather tanned with both tannins reached grade 1 in the blue scale. The blue scale has 8 levels, where level 1 is the weakest, that is, high fading probability and level 8 is the strongest. The leather tanned with Red Angico and Black Jurema will not hold the original color if exposed to natural light and heat.

There was no difference in the retraction of leather tanned with Red Angico in relation to the direction of the sample (longitudinal and transversal). However, the leather tanned with Black Jurema showed difference regarding the direction of the sample, with greater retraction in the transversal direction, according to standard ABNT NBR 15170 (2013) (Table 7).

Table 7. Mean values and standard error for retraction temperature assay (%).

Species	Retraction Results (%)	
	Parallel to backline	Perpendicular to backline
Red Angico	34.1±1.8	33.9±0.4
Black Jurema	26.9±2.1	35.1±0.8

n = 3 (number of replicates).

Perpendicular to the backline, the leather tanned with Black Jurema shrank less when compared with the same direction of leather tanned with Red Angico tannin, and the opposite occurred in the transversal direction.

4 - Conclusion

Red Angico and Black Jurema are condensed tannins and have similar percentages of tanning agents in their barks. Their tanning potential was sufficient to tan the sheep hides.

However, Red Angico was the extract with the greatest tanning potential, which provided leather with more volume and greater tear resistance (ABNT NBR ISO 3377-1 and ABNT NBR ISO 3377-2). However, the leather tanned with Red Angico was dark brown, a feature that might influence the tanning process with light colors.

The leather tanned with Red Angico and Black Jurema tannins presented low color fastness (grade 1 in the blue scale).

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