GSC Advanced Research and Reviews

eISSN: 2582-4597 CODEN (USA): GARRC2

Cross Ref DOI: 10.30574/gscarr

Journal homepage: https://gsconlinepress.com/journals/gscarr/

(RESEARCH ARTICLE)

Appropriateness of *Anogessus leiocarpus* leaves and bark as vegetable tannins traditionally used in leather making in Sudan

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GSC Advanced Research and Reviews, 2023, 14(01), 007–013

Publication history: Received on 16 November 2022; revised on 24 December 2022; accepted on 27 December 2022

Article DOI: https://doi.org/10.30574/gscarr.2023.14.1.0371

Abstract

Chrome tanning industry is dominated globally owing to its high versatility in quality leather production. However, Environmental impacts of chromium have shifted the interest of present study to chrome-free options. Vegetable tannins have been proven to be environmentally safe producing good quality leather with comparable properties as that of chrome tanned leather. As such, scarcity of vegetable tannin supply demands characterization of non-commercialized sources locally available to feed local tanners. A simple extraction technique was used with different temperature 35, 50, & 85 °C. Leaves and barks from *Anogessus leiocarpus* grown in Sudan can produce commercially acceptable tannins in terms of extract yield, tannin, total phenolic, flavonoid contents, and crosslinking ability comparable to the extract from *A. mearnsii* barks, which is a worldwide known to be commercial tannin source. Results shows that temperature influences on extraction yields and tannin content was low, except for extract from *Anogessus leiocarpus* leaves that has shown an increase pattern with raise in temperature. Total phenolic and flavonoid content varied insignificantly with increase in extraction temperature, except for total flavonoid content of extract from *Anogessus leiocarpus* leaves that observed to be high at 50 °C (30.7). Variations in extract properties between extracts from plant parts studied in this work were significant. Tensile strength values of tanned skin with leaves extracts are higher than that tanned with barks. On the other hand, tanned skin with leaves extract produced greater skin elongation 40.6±0.35 compared to barks extract.

Key words: Vegetable tannins; Hydrothermal stability; Chemical properties; Leaves; Barks

1. Introduction

Vegetable tannins, are polyphenolic compounds of vegetal origin with the property to precipitate proteins. Application of this tannins in the past was to stabilize animal skin protein against deterioration [1]. So, the process used vegetable materials can be defined as the handling of animal skin through washed, limed, dehaired, fleshed, delimed. The consequence is a stable and non-deteriorated material, resistant to putrefaction caused both by microorganisms and heat, when wetted. This is due to the chemical bonds established between collagen, the main constitutive protein of skin, and the tannins present in the vegetable materials. Collagen stabilization occurs when 15% to 40% of tannins, per dry weight of skins, are absorbed and incorporated into the collagen fibers matrix, depending of the type of leather produced [1–5].

In developed countries vegetable tanned leather was very much demanded due to its versatility. Its properties, ranging from flexible to rigid, depend on the raw materials and tanning methods. It was a fundamental material for the production a wide range of artefacts such as footwear, garments, book bindings, saddlery, wall-hangings, furniture upholstery, cases coverings, carriages or liquids containers [6,7]. Beyond its utilitarian function, it was also used as support material for artistic and decorative paintings, wall hangings or screen coverings [8-10]. Therefore, vegetable

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tanned leather is the most common type of heritage leather found in museums and collections [11,12]. In this research work, the suitability of *Anogessus leiocarpus* (leaves & Bark) *as* vegetable tannins for making leather was evaluated with objective of producing good quality leather with comparable properties.

2. Material and methods

2.1. Materials

Anogessus leiocarpus Leaves and bark were collected from EL Dalang forest South of Kordofan State in Sudan. Hide powder and pelt samples were donated by Khartoum Tannery in Sudan. All chemicals used were of analytical grade and for tanning trials, commercial grade chemicals were used.

2.2. Extraction of Tannins

Collected samples of leaves and barks were dried under shed for couple of weeks and cut into small pieces. The chipped pieces were ground in a milling machine (Retsch SM 2000) and sieved by 1 mm size mesh. Therefore, samples of leaves and barks of particle size <1 mm were collected separately for extraction. 40 g of milled leaves and barks were soaked in 400 mL of distilled water in a glass beaker covered with aluminum foil to prevent water evaporation. The mixture was placed on water bath maintained at a chosen temperature (30, 50 and 85 ^{o}C). Stirring of the sample mixture was maintained using magnetic stirrer connected to the beaker's opening through small hole made on the aluminum foil. Extraction process continued for 4 h, then the filtrates were collected. The residues were subjected to the second extraction using 400 mL distilled water for 4 h. First and second filtrates were mixed and concentrated at 40 ^{o}C under vacuum using rotary evaporator (Rotavapor R210) and then lyophilized. Resultant extract powder was analyzed for yield of extract, tannin content, non-tannins, total phenolic content and total flavonoid content.

Extract yield was calculated by the following equation

$$\% \text{ Extract yield } = \frac{\text{Extract obtained (g)}}{\text{Amount of moisture content}} \text{X } 100$$

2.3. Tannin content Determination

Bell method as described by Atkin and Thompson (1937) [13] was used for determination of Tannin content. Tannin solution was de-tanned by lightly chromed Powder batch number 'VK 383'. A little dry cotton-wool was placed in the upper part of the bell to prevent hide powder from passing through the capillary. The neck was fixed with rubber stopper carrying capillary glass tube bent twice at right angle. Subsequently the bell was filled with 7 g of hide powder and pressed outward onto the bell's wall to block channels that may allow tannin solution to pass. The filter bell so prepared was placed in 200 ml beaker and the latter was filled with tannin solution and placed in the water bath maintained at 30^{o}C. After the tannin solution being absorbed by hide powder up to the neck, gentle suction was applied to the capillary limb until liquid flows out slowly at the rate of 8-10 drops per minute. The de-tanned solution gave no turbidity with gelatin-salt reagent. The first 30 mL of de-tanned solution was discarded and 50 mL of the next 60 mL was evaporated and dried to constant weight to determine non-tannin content.

Tannin content was calculated as follows:

Tannin content = Soluble substances -non tannins

2.4. Determination of total phenolic content

Total phenolic was carried out as previously described [14]. 5 mL of 10% Folin-Denis reagent was added in 0.2 mL of extract solution and mixed well. After 6 min, 4 mL of 7.5% sodium carbonate was added. The mixture was diluted to 25 mL with deionized water and incubated for 90 min. Absorbance was recoded at 760 nm using UV-VIS spectroscopy (Evolution 201). Gallic acid was used to obtain calibration curve and the concentrations used were 50, 75, 100, 125, 200 mgml^{-1}. Total Phenolic Content was expressed as mg Gallic acid equivalent per g dry weight of the sample and then presented as percentage based on dry weight.

2.5. Determination of leather properties

The limed pelts were tanned with 22% of each extract using conventional tanning method to assess its performance in hydrothermal stability, mechanical properties, and chemical properties.

2.5.1. Chemical Analysis of leather

Leather was cut into small pieces to pass through a screen with circular perforations of 4 mm. The pieces were thoroughly mixed and brought to a state of homogeneity by keeping them in a closed container for at least overnight. Then Moisture content, Fat content, Insoluble ash, hide substances, volatile substances, dichloromethane-soluble substances, and Water soluble % was determined [15].

2.5.2. Physical Analysis of leather

Measurement of thermal shrinkage temperature

Hydrothermal stability was assessed by measuring shrinkage temperature and denaturation temperature by using conventional shrinkage temperature test and DSC method, respectively. Differential Scanning Calorimetry analysis is done for assessing denaturation temperature, by taking 6 mg of wet leather sample placed in an aluminum pan. Temperature scans were run from 10 to 125 ^{o}C with a rate of 5 ^{o}C per minute. From the endotherm's onset temperature (T peak) and peak temperature (T onset) were calculated. On the other hand, shrinkage temperature is carried out by using wet samples with dimensions of 3-5 cm were clamped and immersed in water, which in turn was stirred vigorously using magnetic stirrer. The temperature of the solution was gradually increased and the temperature at which the sample shrinks by one third of its original length was recorded. Testing was repeated twice per each sample.

Measurement of Tensile strength

Measurements of tensile strength was done using an Instron testing machine (model 1112 and 0–500 g load cell) designed for a liquid cell attachment. The sensitivity of the load cell was 1% at the maximum range. The specimen length was 1 cm and the elongation rate used was 0.5 cm min^{-1}. The tensile strength in water medium at room temperature were calculated [16].

$$\text{Tensile strength } = \frac{\text{Maximum breaking load}}{\text{Cross sectional area}}$$

3. Results and discussion

3.1. Property of plant extracts

Extraction was carried out in varying temperature from 35,50, & 85 ^{o}C. Extract obtain at each temperature was analyzed to determine extraction yield, tannin content, total phenolic and flavonoid content, as well as crosslinking ability. The temperature that gave maximum values for all features was chosen to extract vegetable tannins for further studying of tanning and tanning performance.

3.2. Extraction yield

Total phenolic, tannin, and flavonoid content were influenced by temperature applied during extraction of tannins. Temperature is an important parameter to consider, because it regulates extract yield as well as the quality of extracts in terms of phenols, tannin, flavonoids, and non-tannins contents [17]. It has been reported that, high temperature improves extraction efficiency because high heat rises permeability of cell wall and solubility of extractable matters, while reducing viscosity of the solvent [18]. On the other hand, studies have revealed that extraction at high temperatures leaches undesirable compounds such as gums that affect the quality of leather [19-21].

Results shows that temperature effect on extraction yields and tannin content was low, except for extract from the *Anogessus leiocarpus* leaves that has shown an increase with raise in temperature as shown in Table 1. Total phenolic and flavonoid content varied insignificantly with the increase in extraction temperature, except for total flavonoid content of extract from *Anogessus leiocarpus* leaves that observed to be high at 50 C (30.7) (Table 1). Variations in extract properties between extracts from plant parts studied in this work were significant. This is due to the fact that extracts from different plant parts have different chemical composition and molecular structures [22,23]. On the other hand, *Anogessus leiocarpus* bark gave less extract yield than that of *Anogessus leiocarpus* leaves (Table 1). Tannin, total phenolic, and total flavonoid contents of extract from *Anogessus leiocarpus* barks were comparable to those of *Anogessus leiocarpus leaves*.

Table 1 Effect of extraction temperature on total phenolic, flavonoid, tannin, and extracts yield of plant

Parameters	**Leaves**			**Barks**		
	35 °C	**50°C**	**85 °C**	**35 °C**	**50 °C**	**85 °C**
Phenols	19.9	22.4	60.6	9.6	9.6	9.7
Flavonoids	8.6	30.7	25.5	1.9	12.0	18.0
Tannin	15.5	176	20.8	10.9	12.6	13.5
Extraction Yield	35.6	37.7	48.8	15.6	16.8	15.4

Howes, 1953 [24] recommend that plants to be of commercial interest as a tannin source, the ratio of tannin/non-tannin (T/NT) should be equal or more than 1. *Anogessus leiocarpus* barks displayed lower (T/NT) compared to *Anogessus leiocarpus* leaves (Table 2), but above the suggested values indicating that the extract is suitable for vegetable tanning [24,25].

Table 2 Effect of extraction temperature on Tannin/non-tannin (T/N) ratios of plant

Temperature	**Leaves**			**Barks**		
	Tannin	**Non-Tannin**	**Extraction ratio**	**Tannin**	**Non-Tannin**	**Extraction ratio**
35 °C	12.5	9.8	1.27	7.5	7.4	1.01
50 °C	15.8	11.5	1.3	9.6	9.0	1.06
85 °C	20.8	13.6	1.5	14.5	11.8	1.22

3.3. Leather chemical characteristics

Whole leather samples showed desirable results of chemical properties. Low water solubility observed in all sample indicates that leather tanned with tannins from studied plants have good water resistance (Table 3). Degree of tannage in both leather samples was almost similar to that of leather tanned with *Acacia mearnsii* (Table 3) and it falls in the recommended value for vegetable tanned leather, 50-95% [15]. The chemical properties of *Anogessus leiocarpus* leaves and barks tanned leathers are found to be quite normal. The total chemical content satisfies the leather requirement compared with *Acacia mearnsii* tanned leather (Table 3). The free oils and fats present in *Anogessus leiocarpus* tanned leather is (5.5±0.35%) and (7±0.55%) for tanning done by leaves and barks respectively, which are comparable to that of *Acacia mearnsii* tanned leather (Table 3). Low water solubility observed in all sample indicates that leather tanned with tannins from studied plants have good water resistance. The studies thus indicates that vegetable tanning using indigenous *Anogessus leiocarpus* leaves and barks can be easily adopted in the tanneries in Sudan. Their use will reduce imports of chrome and will lessen the attendant pollution. Cost benefit studies may also show considerable benefits for non-Sudanese users of *Anogessus leiocarpus* plant who may not have access to another tanning agent. Depending on the particular quality needed in the final leathers, *Anogessus leiocarpus* tannin can either be used as a pre-tanning or retanning agent [26].

Table 3 Chemical properties of leather tanned with *Anogessus leiocarpus* leaves & barks

Parameter	***Acacia mearnsii* bark**	**Tanned skin by *Anogessus leiocarpus* leaves**	**Tanned skin by *Anogessus leiocarpus* barks**
Moisture content, %	13±0.15	12.5±0.05	12.8±0.25
Fat content, %	6.5±0.75	5.5±0.35	7±0.55
Ash, %	14.9±0.45	15±0.45	20±0.75
Hide substances, %	60±0.15	65±0.68	50±0.74
Tannage degree	60.5±0.35	60.4±0.15	59±0.25
Water soluble, %	4±0.65	3.6±0.45	5±0.65
pH	7±0.01	6±0.02	6±0.05

3.4. Leather physical characteristics

3.4.1. Mechanical properties of leather

The mechanical properties of samples of the leather are presented in Table 4. Tensile strength of the leather tanned with *Anogessus leiocarpus* leaves is more or less the same as the tensile strength of the leather tanned with *Acacia mearnsii* extract, but elongation at break for *Anogessus leiocarpus* leaves tanned leather is marginally higher than that of *Acacia mearnsii*, in agreement with hydrothermal stability results. On the other hand, softness of leather tanned with *Anogessus leiocarpus* leaves displayed lower softness value than *Acacia mearnsii*, though the difference is not large. Leather tanned with *Anogessus leiocarpus* bark extracts gave the lower values in all parameters compared to *Acacia mearnsii,* these outcomes support the findings described in present study, which confirmed low ability of *Anogessus leiocarpus* bark extract to crosslink all collagen molecules due to less tanning content as well as total phenolic and flavonoid content, hence affecting the mechanical properties as well.

Table 4 Mechanical properties of leather samples tanned with extracts from *Anogessus leiocarpus* leaves & barks

Parameter	***Acacia mearnsii* bark**	**Tanned skin by *Anogessus leiocarpus* leaves**	**Tanned skin by *Anogessus leiocarpus* barks**
Tensile strength (Nmm2), %	10±0.35	10.5±0.35	7.8±0.25
Elongation at break, %	40±0.35	40.6±0.35	32±0.55
Softness (mm) %	1.0±0.05	2.6±0.45	1.5±0.75
Water vapor permeability mg/cm2/h	4±0.05	6±0.05	8±0.05
Water uptake during water vapor permeability mg/cm2 /h	70.0±0.05	80.0±0.05	60.0±0.05

3.4.2. Hydrothermal stability analysis

Tanned leather samples with *Anogessus leiocarpus* leaves & barks were examined for measurement of hydrothermal stability. Differential scanning calorimeter is used for measurement of shrinkage temperatures (T_s). Results disclosed that extracts of *Anogessus leiocarpus* leaves performed better in terms of hydrothermal stability than that of *Acacia mearnsii (*Table 5) [20,27].

This enhanced hydrothermal stability of *Anogessus leiocarpus* leaves tanned collagen is owing to new crosslinks formed and consequent changes in the tertiary structure of collagen. Hydrothermal stability of leather tanned with extract from *Anogessus leiocarpus* bark was comparable to that of leather tanned with *Acacia mearnsii*, except that T_s and Temperature at maximum tension (T_t) gap was wider than that of the latter species. These results correlate with the observation made on analysis of crosslinking ability of extracts.

Table 5 Shrinkage temperature and temperature at maximum tension of leather samples tanned with extract from *Anogessus leiocarpus* leaves & barks

Parameters	**Shrinkage temperature (Ts),** ℃	**Temperature at max. tension (Tt),** ℃
Native	68±0.32	70±0.55
Acacia mearnsii bark	89±0.32	96±0.55
Tanned skin by *Anogessus leiocarpus* leaves	90±0.63	>98±0.57
Tanned skin by *Anogessus leiocarpus* barks	86±0.45	>94±0.25

4. Conclusion

In the current research work, surveys were made to study appropriateness of tannins from Sudan local trees used traditionally by local leather industries to make leather. A simple extraction technique was used with temperature of

35, 50, & 85 °C. Leaves and barks from *Anogessus leiocarpus* grown in South of Kordofan State- Sudan can produce commercially acceptable extract in terms of extract yield, tannin, total phenolic and flavonoid contents, and crosslinking ability almost comparable to that of extract from *Acacia mearnsii* barks, which is a worldwide known to be commercial tannin source. That means, *Anogessus leiocarpus* abundantly available in Sudan with rare use can potentially be cultivated for production of tannins. This investigation provides useful information for possible commercialization of local plants used by local tanners as tannin source for increasing supply of tannin towards development leather sector in Sudan and beyond.

Compliance with ethical standards

Acknowledgments

The authors are grateful to Bahri University and forest National cooperation, for financial support and national Centre for research for giving the possibility to use the resources and facilities of their laboratory.

Disclosure of conflict of interest

Authors have declared that no conflict of interests exists.

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