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THE TANNING POTENCY OF LANDOLPHIA OWARIENSIS ON SHOE UPPER LEATHER

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ABSTRACT

Landolphia owariensis belongs to the family Apocynaceae and its roots are commonly used as medicinal plant for the treatment of malaria and as purgative. The leaves extract is antimicrobial and the stem extract is used as a vermifuge. The phytochemical analysis of L. owariensis indicated secondary plant metabolites such as tannins, and flavonoids. The presence of tannins and flavonoids makes it imperative to conduct a formal study of its tanning potentials. This paper is reporting the application of phytochemical and classical methods of tannin analysis, and the use of the extracts for tanning purpose. The result of the phytochemical analysis showed the presence of tannins, saponins, fat and oils; while the classical analysis showed that the extract contains tans, non-tans, total soluble and moisture. The tanning extracts were used to tanned goat skins and the resultant leather shows favorable standard value for shrinkage temperature, tensile strength, and ball burst.

***Key words**: Landolphia owariensis, phytochemicals, shrinkage temperature*

Introduction

Landolphia owariensis is a common African plant that has been found useful due to its therapeutic potentials (Owoyele *et al.,* 2002). The plant contains abundant white latex which may become pinkish on exposure, sticky and coagulable on prolong boiling to a project called paste rubber. It belongs to the family of Apocynaceae and known locally by various names in Nigeria: Igbo-Eso/Uto, Yoruba–Mba, Hausa–Ciiwoo and English-white vine rubber. It is commonly found in the rain forest region of Nigeria. It is one of the plants whose leaves, barks and roots are used for the treatment of many ailments (Shobha, 2011). The decoction from the leaves is used as purgative and to cure malaria. The aqueous methanolic and chloroform extract of L. owariensis leaves have antimicrobial activities (Owoyele *et al.,* 2002; Nwaogu *et al.,* 2007). *Landolphia owatriensis* leaves have been reported to contain various secondary plant metabolites of medicinal value including tannins, alkaloids, saponins and flavonoids (Trease and Evans, 1996; Ahsan, *et al.,* 2015).The determination of tannins from vegetal products is of paramount importance to the leather industry. Methods for the determination of tannins may include:

a- A gravimetric method based on the precipitation of tannins with copper acetate.
b- Colorimetric method.
c- High performance liquid chromatography (Paul *et al.,* 2002).
d- Titrimetric method (Atanassova and Christova, 2009).
e- Shakes method (Mansoor *et al.,* 1988; Palici *et al.,* 2005).

Due to the relative abundance of landolphia owariensis and its medicinal application, it becomes very imperative to identify the presence of tannins, quantity and relevant application in the leather industry and its effect on the physical properties on the resultant leather which forms the basis of this study.

Plate 1.0: Landolphia owariensis Plant

Materials and Methods

Plant Material: Collection and preparation

Fresh leaves sample of landolphia owariensis (ciiwo) were collected from Chikun local government area of Kaduna State and identified at the herbarium of the Department of Biological Sciences, Ahmadu Bello University Zaria. Landolphia owariensis leaves (A1 and A2) were rinsed with water, sundried for 10days before they were grounded into powdery form (Gary, 2004) using Procter milling machine and sieved through using 0.2mm mesh and kept in a polythene bag. Two wet-salted goatskins of good quality (medium size) were purchased from Samaru market in Sabon Gari local government area of Kaduna State for the tanning analysis.

Extraction Procedure
A quantity (10g) of the powdered leaves was immersed in 500ml of n-hexane and subsequently extracted using soxhlet extractor. The n-hexane extract was concentrated using rotary evaporator and then preserved at 5^{o}C in an air tight bottle until used for phytochemical screening (Ukoha *et al.,* 2001).

Phytochemical Screening: The extract was screened for the presence of flavonoids and tannins.

Test for Flavonoids: A quantity (0.2g) of the extract was heated with 10ml of ethylacetate in boiling water for 3min. the mixture was filtered differently and the filtrates used for ammonium test (Ukoha *et al.,* 2001).

Ammonium Test: A quantity (4ml) of the filtrate was shaken with 1ml of dilute ammonium solution (1%) the layers were allowed to separate (Ukoha *et al.,* 2001).

Test for Tannins: A quantity (2g) of the extract was boiled with 5ml of 45% ethanol for 5min. The mixture was cooled and filtered. The filtrate was subjected to ferric chloride test.

Ferric Chloride Test: A quantity (1ml) of the filtrate was diluted with distilled water and added 2 drops of ferric chloride (Ukoha *et al.,* 2001).

Tanning Recipe: Standard shoe upper leather recipe was used with little modification to suit the present study from raw skins to crusting of the leather (Sakar, 2002).

Shrinkage Temperature: Procedure: This was carried out on the wet-blue leather sample. About 5.5ml ± 0.5ml of distilled water was transferred into a glass tube and the test piece immersed using a glass rod. The test piece end was attached to the test piece holder and the other end of a moveable holder. A thread was attached to balance the pulley and the mass. Sufficient warm water was used to give a depth of 30mm. Water was further heated to maintain the rate of the temperature rise at 2^{o}C± 0.2^{o}C/ min. After 30s interval the temperature and the corresponding position of the pointer was monitored for the reduction in size of the leather test sample and the final temperature recorded.IUP/16 (JSLTC, 2000).

X-Ray Elemental Analysis of Crude Sample of *Landolphia owariensis* Leaves
This analysis was carried out at the Centre for Energy Research and Training, Ahmadu Bello University Zaria using x-ray spectrophotometer to determine some metals of interest. The samples were grounded in an agate mortar and binder (PVC dissolved in toluene) was added to the sample, carefully mixed and pressed in a hydraulic press to a pellet. The pellet was loaded in the sample chamber of the spectrophotometer at a voltage of 30KV maximum and a current (1MA maximum) was applied to produce the x-ray to excite the sample for (10minutes) and the spectrum from the sample was analyzed to determine the mean concentration of the elements in the sample.

Extraction of Tannins
The extraction was carried out at an elevated temperature with sohxlet apparatus using 625ml methanol for 23g of crushed (0.2mm) Landolphia owariensis leaves. The tannin solution extracted was reduced to 200ml using water bath and consequently oven dried to a constant weight. About 2.0ml of the extract from above was collected and diluted to 10ml using methanol as solvent. This solution was quantitatively transferred into a 250ml conical flask containing 6.25g hide powder and equilibrated for 15minutes, filtered and to the filtrate 1.0g of kaolin was added, shaken and filtered and to a small portion of the filtrate, aqueous gelatin solution (1%) was added to check the absence of tannins. The filtrate was dried to a constant weight which gave the weight of non-tans. The difference in weight of total soluble solids and non-tans gave the weight of tannins present (Mansoor *et al.,* 1988).

Moisture Content in Landolphia O. Leaves
This was determined by equilibrating the leather sample at 20^{o}C and 65 ± 2 %RH, weighed and dried for 24hours at 102^{o}C, cooled in a desiccator and weighed again. The material lost is considered to be the moisture content (Hallebeck, 1994).

Measurement of Tensile Strength and Elongation at Break

Principle: The test piece is extended at a specified rate until the forces reach a predetermined value or until the test piece breaks.

Procedure: The dimensions and thickness of the cut leather samples were measured using Vernier calipers to the nearest 0.1mm. The jaws of the tensile strength testing apparatus were set at 50mm apart and the leather sample clamped with the grain surface in one plane. Force was applied to the test piece until breakage was observed, the highest force exerted as the breaking force (N/mm^2) was recorded, IUP/4 and IUP/6 (JSLTC, 2000). The instrument used is the material testing machine with an inbuilt type of 500N with Model number 167998/2005/E.

Measurement of Distension and Strength of Grain by Ball Burst Test

Procedure: A number (3) of upper leather discs were cut based on official sampling positions. The thickness was measured, grain up in three positions under a load of 500gcm^2 using a standard gauge. This method determines the force required in breaking the strength of the grain during lasting operation of shoe uppers. Muver electronic lastometer with model number 5077.ET attached with Epson (EPL-6200) printer was used for this analysis, IUP/8 (JSLTC, 2000).

Results and Discussions
The results for this study are shown below:

The shrinkage temperature of a mammalian pelt that has been limed is about 55-60^{o}C(Bailey, 1992; 1998) with

the introduction of landolphia owariensis crude powder offer of 20% and 30% the leather gave shrinkage temperatures of 60 and 62°C; respectively as presented in Table 2.0. The reason for this is that the backbone chains of the molecule exist in an extended form held by hydrogen bonding and the ability of the leather to stretch further translates to the uptake of tanning materials into the fibres. This chemical uptake causes chemical changes in the collagen physically and can be measured using differential scanning colorimetry to appraise the conventional method. The low% of tannins (5.8%) present in the leaves accounts for the low shrinkage temperature recorded even with the application of 20% and 30% offer of the crude extract as presented in Table 3.0.

Table 1.0: Result of Phytochemical Screening of L. Owariensis

Test	Observation	Inference
Flavonoid. 0.2g of sample (L.O) +heat+10ml ethylacetate boil for 3mm and filter. filtrate (4ml)+ 1% dil. NH_3 solution	A yellow coloration at the NH_4 layer observed	Flavonoids present.
Tannins 2g of sample (L.O)+ 5ml of 45% ethanol boil for 5mins. The mixture cooled and filtered. filtrate (1ml) + H_2O of 2 drops + $FeCl_3$	A transient greenish to black coloration observed	Tannins present

Table 2.0: Hydrothermal Stability of L. Owariensis at Different Concentrations.

Concentration	L. owariensis °C A
30%	62
20%	60

Table 3.0: Analysis of Vegetable Tanning Materials

S/N	Constitution (%)	Landolphia O
1	Tannins	5.8
2	Non Tans	10.3
3	In-solubles	75.9
4	Moisture	8.0
5	pH	3.6

The tannin content in *L. owariensis* has been investigated. The results showed the following: tannins 5.8%, non-tannins 10.3%, insoluble 75.9%; moisture 8.0% at pH of 4.2. This result indicates that the tannin content was low which accounts for its possible application in traditional medicines, natural drugs, pharmaceutical industries and beverages (Owoyele *et al.,* 2002; Shobha, 2012). Fresh leathers contain about 10-14 % moisture although older leathers may have less than 10% which is in agreement with the result obtained. Sometimes leathers contain hygroscopic materials which might exaggerate the amount of moisture content (Hallebeck,1994).More so, stiffness or brittleness of the leather is caused by fluctuation in moisture content as a result of temperature and relative humidity changes (Florian,1985).

The result of elemental analysis of crude *L. owariensis* From Table 4.0 shows the presence of some metals and their various concentrations like K (1.50%), Ca (1.81%), Fe (242ppm), Mn (788ppm) and Ni (0.62ppm) *L. oweriensis*, the high amount of iron in the elemental analysis accounts for the darkening of vegetable tanned leathers during production or ageing and can be cleared oxidatively by re-converting the quinone present to phenol. *L. owariensis* shows low concentration of K (1.50%). The high concentration of Fe in *L. owariensis* may be from the soil on which the plant grows. These metals especially Fe, Mn and Ni if present in high concentration could leach into the resultant leather during tanning and consequently bio-accumulate in the human skins during usage as footwear to cause cancer and other related diseases.

Table 4.0:Result of Raw Sample Showing Different Concentrations of Metals In L.Owariensis.

Elements	Concentration (ppm) L. owariensis
K	1.50%
Ca	1.81%
Fe	242
Mn	788
Ni	0.62

The significance of tensile strength and the percentage elongation is that it helps in determining the physical properties of leather and also the extent to which particular leather can be stretched or pulled when in use and to judge the performance of the leather produced. Although the result of tensile strength was good except for grain at crack. The good result might be connected with the extra percentages of crude tannins applied during retanning which have a correctional effect on the shrinkage temperature earlier recorded (60-62 °C). Consequently the fat-liquour used has some tanning effect in lubricating the leather fibre and increasing the tensile values of the leather samples. The results for tensile strength of the leather samples are presented below with standard values (BASF) in Table 5.0.

Table 5.0: Results for Tensile Strength

Iup6	A1	A2
Strength at grain crack (N/mm^2)	10.20	10.14
Standard Values	>25	>25
Elongation at crack (%)	65.1	60.1
Standard Values	>40	>40
Strength at break (N/mm^2)	20.1	16.20
Elongation at break	84.41	79.01
Standard Values	>40	>40

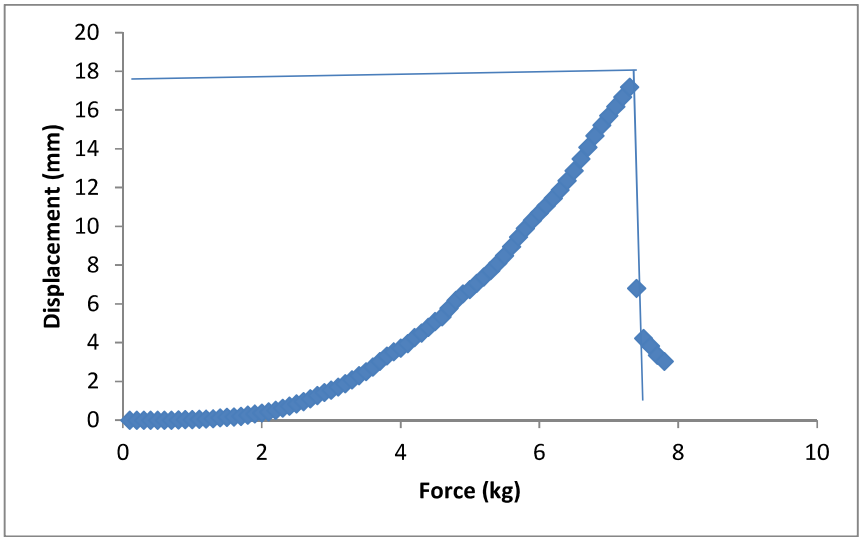

Figure 1.1: Graph showing the results of ball burst (Lastometer) using 30% L. owariensis

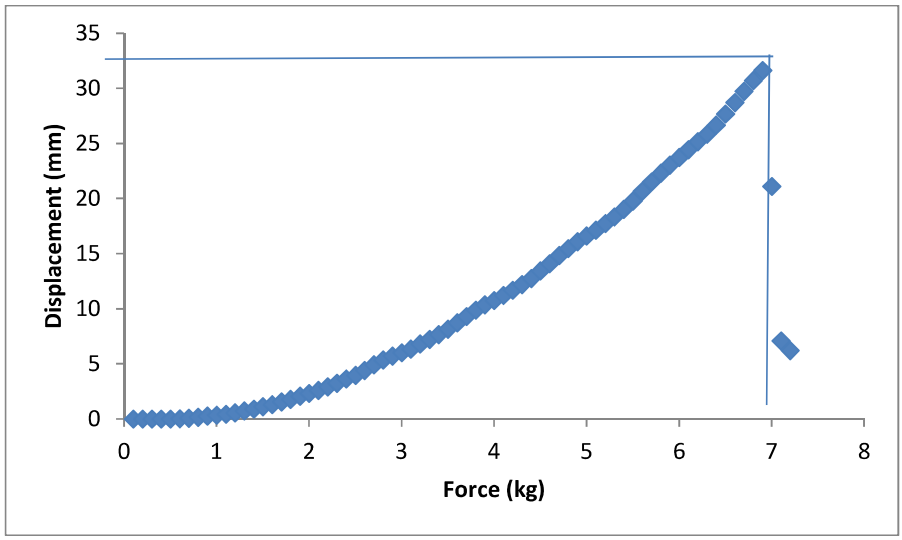

Figure 1.2: Graph showing the results of ball burst test (Lastometer) using 20% L. owariensis

The lastometer test helps in determining the grain property of the leather sample in relation to the applied force during usage which account for grain crack and burst as presented in Figures 1.1-1.2 above, conformed to standards (http://www.basf.com/leather).

Conclusion

This study has shown that ***L.owariensis*** when used in tanning has a very low tannin content which translates to low shrinkage temperature and should be used in combination with other tannin materials. The tensile strength and lastometer tests could be improved on when the percentage of tannin extract is increased and carefully monitored during production.

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