

# Evaluation of Potential Application for Sunt Pod Extracts (*Acacia Nilotica*) in Leather Tanning

by

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## Abstract

The current investigation was carried out to evaluate the efficiency of using sunt, *Acacia nilotica*, pods extract in leather tanning. Skins from 16 Barki rams aged 12-18 months were cured and prepared for tanning using sunt pod extract. The sunt pods were collected and dried at 25 °C for 5 days. Thereafter, the dried pods were ground by a 0.3 mm fineness grinder and were further subjected to the extraction procedure. Three chemical additives, namely NaOH, Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> were used for the extraction at 70 and 90°C. The influences of both types of chemical additive and extraction temperature on extraction yield were determined. The extract characteristics in terms of stiasny number, hide powder, tannins, non-tannins and total phenol contents were also analyzed. The results showed that increasing extraction temperature increased (P<0.05) extraction yield and improved the quality of the extract regardless of chemical additive type. Meanwhile, the extraction using either Na<sub>2</sub>SO<sub>3</sub> in aqueous solution or by water at 90°C yielded the best extract characteristics. The elevated concentrations of condensed and hydrolysable tannins obtained in our results point to the possibility of utilizing sunt pod extract in tanning or re-tanning of leather rather than using traditional tanning reagents.

## Introduction

The term “tannin” was first introduced in 1796 and came from the use of these compounds in tanneries. Tannins containing plant extracts have been used to process animal skin into leather since ancient times. Tannins are water-soluble high molecular

weight polyphenolic compounds rich in phenolic groups. Industrially, tannins are used in the production of leather, adhesive material, dyestuff and ink. Also, due to their astringent properties, tannins are used as medicinal materials which promote rapid healing and formation of new tissues on wounds and inflamed mucosa.<sup>1</sup>

New tannages for the 21<sup>st</sup> century are aiming to decrease the tanning pollution effect by using environmental-friendly tanning procedures. In this regard, vegetable tanning is considered one of the recent tanning techniques used worldwide. However, the currently available vegetable tanning agents are insufficient to tan the current supply of hides.<sup>2</sup> Therefore, the leather industry in Egypt relies mainly on chrome tanning, as well on mimosa or quebracho tannin extracts.

In Egypt there are many indigenous and exotic plant species, which contain variable concentrations of tannins. Some of these plants have been analyzed, although no systematic screening has been completed.<sup>3</sup> *Acacia nilotica* (Sunt in Arabic) is a member of the subfamily Mimosoideae of Leguminous trees.<sup>4</sup> The tree is characterized by the long white spines, yellow head inflorescence and the gray necklace-like pods.<sup>5</sup> It has multiple uses in Africa and many Arab countries because it is abundant.<sup>3</sup> Sunt is traditionally used for tanning in tropical Africa in a primitive way, and is one of the most important tanning materials in Northern India.<sup>6,7</sup> Although both pods and bark of *Acacia nilotica* contain high concentrations of tannins, the tannin percent using pods extract is more efficient than that extracted from the bark, and ranges from 26 - 70%.<sup>3,5,6,8,9</sup>

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Extraction solvent, temperature, time and alkaline additives are important factors when extracting phenolic compounds, due to their impact on both extraction yield and extract quality.<sup>10-14</sup> However, sulfitation is one of the oldest techniques used for extraction of tanning reagents, increasing the extraction yield of tannins with improved solubility and lower viscosity.<sup>14</sup> The use of solvents other than water on an industrial scale can be problematic especially in the areas of pollution, recycling and cost.<sup>12,13</sup>

Generally in vegetable tanning raw materials, the low-molecular tanning substances are converted into higher condensed products when plant life stops. Therefore, either extraction with water only or after adding small quantities of sulfites enough to yield weakly acid or even weakly alkaline extracted liquors is hampered. Alkali or more substantial quantities of sulfites in weakly acid or alkaline medium dissolve the high-molecular tanning materials. This may result in a reduction of the molecular size or their sulfonation. Therefore the alkaline extraction is a more gentle way than any violent processes, such as, extraction under pressure. Moreover, sulfite-alkali mixtures for example sodium sulfite and sodium hydroxide, are used to improve the extraction conditions for a reaction between the sulfite and the tanning materials.<sup>15</sup> On the other hand according to literature<sup>16</sup> when extracting the bark with weak alkaline solutions or in the presence of sulfite and bisulfite, the pyran rings of polyphenols are partly cleaved with the formation of carboxylic groups and sulfonic acids. Therefore, the solubility of phlobaphens increases considerably.

The current investigation aimed to evaluate the possibility of using *Acacia nilotica* pods extract, obtained by different reagents at different temperatures, in leather tanning. The extract characteristics in terms of stiasny number, hide powder, tannin, non-tannins and total phenol contents were also analyzed.

## Experimental

### Raw Material

Sunt pods were collected from Shalatin region in south of Egypt, and were directly transported to Mariout Research Station in Alexandria, where they were dried at  $25\pm 2^\circ\text{C}$  for five days in an open and shaded place without using any thermal drying methods. Thereafter, the dried sunt pods were ground by a 0.3 mm fineness grinder and stored in paper bags until extraction.

### Extraction Procedure and Experimental Design

Extraction steps were performed in the chemical laboratory of the Institute of Textile and Leather Technology, Reichenbach, Germany. Moisture was determined in the ground material, then extraction steps were done using either hot water only or

after adding different chemical additives.<sup>11,13</sup> A 2-L Pyrex glass reactor integrated with mechanical stirring and automatic temperature control was used for extraction. The solid / liquid ratio was maintained constant at 1/10 (w/w). The extraction procedure was conducted either by water only or after adding sodium hydroxide, sodium sulfite or sodium carbonate in aqueous solution to 0.25% dry plant material weight. The extraction temperatures were set at 70 and 90°C. Ground material and water were mixed at room temperature, heated and, once the selected temperature was attained, the chemical additive was added and contact timing started. After one hour the warm suspension was vacuum filtered, whereas the solid residue was washed with water. The extracts, together with the first water washings, were further dried in an oven at 70°C. The extraction yield was calculated as the percent of weight loss of the starting raw material.

### Total Phenol and Tannins Content

Total phenol content was determined by the Folin-Ciocalteu method.<sup>17</sup> Briefly, 0.5 mL of an aqueous solution of the extract, 2.5 ml of Folin-Ciocalteu reactive, previously diluted with water (1:10, v/v) and 2mL of a 75 g/l sodium carbonate aqueous solution were added. The mixture was kept at 50°C for five minutes and, after cooling, the optical density was measured at 720 nm. The phenols content was calculated as a tannic acid equivalent (TAE) from the calibration curve of tannic acid standard solutions (2–40 g/ml) and expressed as g TAE/100 g of extract based on dry basis. Polyvinylpyrrolidone (PVPP) was used to bind tannin-phenolics for measurement of tannins, then non-tannins were determined and tannins were calculated.

### Hide Powder Test

Samples (400 mg) of each extract were dissolved in 100 ml of distilled water. Slightly chromated, previously dried hide-powder (3 g) was added and the mixture was stirred for one hour at an ambient temperature. The suspension was filtered without a vacuum through a sintered glass filter. The weight gain of the hide-powder was expressed as a percentage of the initial weight of the starting material.<sup>13</sup>

### Stiasny Number

Samples (100 mg) of each extract were dissolved in 10 ml of distilled water. 1 ml of 10M HCl and 2 ml of formaldehyde (37%) were added and the mixture heated under reflux for 30 minutes. The reaction mixture was filtered through a sintered glass filter while hot. The precipitate was washed with hot water (5x 10 ml) and dried. The yield of tannin was expressed as a percentage of the initial weight of the starting material.<sup>13</sup>

### Fourier Transform Infrared Spectrometry (FTIR)

The Bruker alpha FT-IR Spectrometer was used to analyze the changes in the chemical structure of the different plant

material extracts. Low quantities of the extracts were used in the solid phase and scanned directly on the instrument stage by diamond ATR equipment.

#### Mass Spectroscopy (MS)

One gram of the water extracts was sent to the Institute of Inorganic and Analytical Chemistry, Jena, Germany. The samples were scanned with the Thermo Finnigan MAT 95XL mass spectrometer to determine the elemental composition of a sample or molecule and also to elucidate the chemical structures of molecules.

#### Determination of Viscosity

The viscosity was measured with a Rheometer MCR 301 and a double-gap measuring system (DIN) from Anton Paar. An aqueous solution with 20% mass fraction of the extract was used at a temperature range from 20 to 40°C.

#### Vis-Spectroscopy and Color Measurement

The reflectance of the crust leather was measured from 400 to 700 nm (spectral interval 10 nm) with a portable SP62 Spectrophotometer (d/8° geometry, aperture 14 mm) from X-Rite which allows to obtain the CIE L\*a\*b\* values.

#### Tanning Procedure

Skins from 16 Egyptian Barki rams aged 12-18 months were cured by salting, then were transported to El-Shafie tannery at El-Max region, Alexandria, Egypt. The cured skins were, then, prepared for the tanning procedure. The same preparation steps were followed for all skin samples throughout application of the initial beamhouse steps, i.e. from soaking to pickling. Thereafter, the pelts were divided randomly into four groups of four samples each, and were tanned with 20% of the different extracts, weighed, then fatliquored, dried and finished.

#### Determination of Leather Properties

All finished tanned leather samples were subjected to a final testing and visual evaluation. Samples were obtained as per ASTM methods<sup>18</sup>. Specimens were conditioned at 20°C ± 2°C and 65% ± 4% RH for 48 h. Physical properties such as tensile strength, elongation percentage at break, split tear strength, static water absorption, permeability to water vapor (PWV) and shrinkage temperature were measured as per standard procedures. Each value reported is an average of four samples (two values along the backbone and two values across the back bone). Chemical properties such as pH, % moisture, % ash, % soluble matter, % hide substances, % fats and degree of tannage have been carried out according to standard procedures.

## Result and Discussions

The data presented in Table I shows the results obtained for extraction yield and extract properties for sunt pods. The highest extraction yield was obtained using NaOH and Na<sub>2</sub>SO<sub>3</sub> aqueous solutions (61.37%), while the lowest was obtained by water extraction (21.66%). The result also clarified that increasing extraction temperature (from 70 to 90°C) resulted in an increase in the extraction yield. Extraction of tannins has been widely utilized on a large scale for application in different industries such as wood adhesive and leather tanning applications. The use of solvents other than water on an industrial scale was considered problematic especially with regards to pollution, recycling and cost.<sup>12,13</sup> Thus, water and different chemical additive aqueous solutions (sodium sulfite, sodium carbonate and sodium hydroxide) at temperatures of 70 and 90°C were used in the sunt pods' extraction.

Furthermore, a decrease in extract characteristics was observed, in all groups, as the alkalinity of the solution increased. Although the extraction yield increased concomitantly along with the increase in pH, the extraction characteristics decreased. This is suggested to be due to increasing the extraction of non-tannins, which, in turn, reduced the quality of the extract. On the other hand, the results showed that increasing the extraction temperature significantly increased extraction yield and improved the extract properties in most cases. In this regard, the highest extract quality was obtained in the water extracts followed by sulfited extracts at the higher extraction temperature (90°C). These results are in agreement with previously published data.<sup>13</sup>

The obtained extraction yield values for sunt pods extracts ranged from 21.66% to 61.37%, whereas the range in literature was from 22.7% to 53.42%. With regard to total phenol, tannins and non-tannins, the results obtained were comparable with previous research.<sup>1,8,19,20</sup>

Typically, the hide powder test gives an indication to the proportion of tannins in the extract which would bind with the skin, whereas the stiasny number gives an indication to the condensed tannins content in the extract.<sup>11</sup> Thus, the obtained hide powder and stiasny number values illustrate that sunt pods contains both condensed and hydrolysable tannins.<sup>20</sup>

#### Extracts Quality Determination

The qualities of the extracts obtained in the current work were determined compared to properties obtained by commonly used vegetable tanning extracts; i.e. quebracho and mimosa extracts<sup>21</sup> (Table I). The obtained results show that quebracho and mimosa extracts were of a higher quality than all sunt pods

extracts because they were higher in the T/NT ratio, hide powder and stiasny number values. Further, at 90°C of extraction, sunt pods extracts with water are of the next best quality, followed by that extracted with aqueous sodium sulfite. Other chemical additive aqueous extracts were of the lowest quality and are therefore unsuitable for use in leather tanning. It is highly likely that more oxidation and decomposition processes take place with a higher pH value. The alkali extracts may be suited for other applications such as additives for adhesives<sup>14</sup>.

Fourier transform infrared was used to study the molecular structure of each extract. The list assignment of the different IR bands is presented in Table II and the infrared spectra of sunt extracts are shown in Figure 1.

The absorption bands for all regions are of medium or weak intensity, except regions (3650-3000 cm<sup>-1</sup>) and (1695-1600 cm<sup>-1</sup>) which are broad and strong. All these regions were recorded previously for tannins extracts.<sup>22-24</sup> Although the extraction method for quebracho and mimosa extracts is unknown, the absorption band 680-600 cm<sup>-1</sup>, belonging to the C-S vibration of sulfonic groups<sup>25</sup>, proved sulfitation in extraction which was also shown with the sunt sulfited extract.

The negative correlation between viscosity and tannins' penetration into skin layer<sup>25</sup> was the reason to measure extract solution viscosity. In addition, a temperature ranging from 20 to 40°C and an extract mass fraction of 20% were chosen because these are the normal conditions used in the vegetable

**Table I**  
**Properties of Different Extracts.**

Material	Additive	Temp. (°C)	pH	Color	Yield (%)	(g TAE/100g extract)*			T/NT	Hide Powder	Stiasny No
						Total phenol	Tannins	Non Tannins			
Quebracho	Unknown		5.83	Reddish-Brown	--	32.98	31.02	1.96	15.84	69.33	97.67
Mimosa	Unknown		5.04	Light-Brown	--	18.24	17.42	0.82	21.83	59.33	82.67
Sunt	Water	70	5.64	Brown	21.66	31.37	20.13	11.24	1.79	42.67	49.00
	Water	90	5.61	Brown	22.35	31.39	23.83	7.56	3.15	60.33	53.00
	NaOH	70	9.43	Dark-Brown	46.79	11.35	3.11	8.24	0.38	30.20	34.33
	NaOH	90	9.50	Dark-Brown	54.11	11.48	4.54	6.94	0.66	33.33	40.67
	Na <sub>2</sub> SO <sub>3</sub>	70	6.16	Light-Brown	36.33	18.87	11.57	7.29	1.59	36.00	33.00
	Na <sub>2</sub> SO <sub>3</sub>	90	6.06	Light-Brown	38.60	19.65	13.58	6.07	2.24	38.33	36.67
	Na <sub>2</sub> SO <sub>3</sub> / NaOH	70	9.73	Dark-Brown	59.81	9.37	3.25	6.12	0.53	35.33	13.00
	Na <sub>2</sub> SO <sub>3</sub> / NaOH	90	9.41	Dark-Brown	61.37	7.47	3.01	4.46	0.68	38.67	13.33
	Na <sub>2</sub> SO <sub>3</sub> / Na <sub>2</sub> CO <sub>3</sub>	70	8.80	Brown	42.61	9.76	4.22	5.53	0.76	23.33	5.33
Na <sub>2</sub> SO <sub>3</sub> / Na <sub>2</sub> CO <sub>3</sub>	90	8.90	Brown	49.11	11.71	6.98	4.73	1.48	24.67	7.67	

TAE: Tannic Acid Equivalent.

\*Numbers calculating based on dry weight of extracts.

tanning industry to avoid skin shrinking<sup>2</sup>. The results of determined viscosity from the different extracts are displayed in Figure 2.

The curve explains that the viscosity of all extracts decreased by increasing the temperature. A similar result was obtained previously.<sup>26</sup> Moreover, the sunt water extract recorded the highest viscosity followed by sunt sulfited, mimosa, and quebracho extracts, respectively. This could be due to sulfitation, which decreased viscosity and increased solubility.<sup>14</sup>

In the current work, electro spray ionization mass spectrometry (ESI-MS) was carried out to determine the major tannins in the obtained extracts. The instrument was operated and scanned from  $m/z$  40 to 2000 in both negative and positive ion mode. Positive mode data was excluded because it contained high noise peaks, whereas negative mode was accepted. The negative ion mode provides a sensitive and selective method for the identification of polar organic compound tannins.<sup>27,28</sup> Mass

spectrum for extracts is shown in Figure 3. In the literature, the results of mass spectrum revealed that quebracho and mimosa extracts are rich in condensed tannins.<sup>29,30</sup>

The peaks at  $M= 643, 915$  and  $1187$  Da in quebracho extract have been reported to correspond to sulfited oligomer

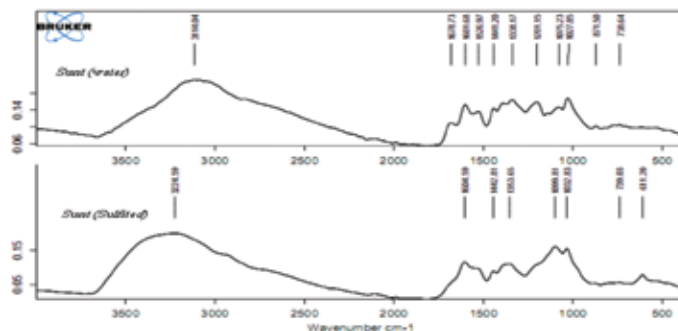


Figure 1. FTIR spectra of different Sunt extracts.

**Table II**  
Assignment of Varying IR Bands of Different Extracts.

Remarks		Absorption peak (cm <sup>-1</sup> )			
Bond	Absorption range (cm <sup>-1</sup> )	Quebracho	Mimosa	Sunt	
				Water	Sulfited
OH stretching	3000-3650	3242	3244	3114	3225
OH bending	1600-1695	--	--	1679	--
		1606	1605	1602	1605
Ring skeletal vibration	1400-1595	1515	1509	1527	--
		1446	1448	1441	1443
Ester group	1175-1390	1368	1308	1338	1354
		1279	1196	1201	--
C-O-C stretching	1000-1200	1158	1154	--	--
		1111	1069	1075	1100
		1033	1024	1028	1033
Aromatic C-H out of plane bending	800-870	--	840	872	--
Ring deformation	700-780	773	--	739	739
C-S vibration of sulphonic group	600-660	643	622	--	611

molecules, while the peaks at  $M= 562, 834$  and  $1106$  Da correspond to unsulfited oligomer molecules for procyanidin dimer, trimer and tetramer, respectively. In mimosa extract, the peaks at  $m/z$  561, 577 and 593 indicate to procyanidindimers, in addition to other peaks at  $m/z$  833, 849, 865 and 879 to procyanidintrimers.<sup>31,32</sup>

Unfortunately, the previous research did not identify the type of tannins in *Acacia nilotica* extract with mass spectroscopy but it was identified as condensed tannin,<sup>33</sup> hydrolysable<sup>34-36</sup> or a mixture of the two types<sup>20</sup> by quantitative method analysis.

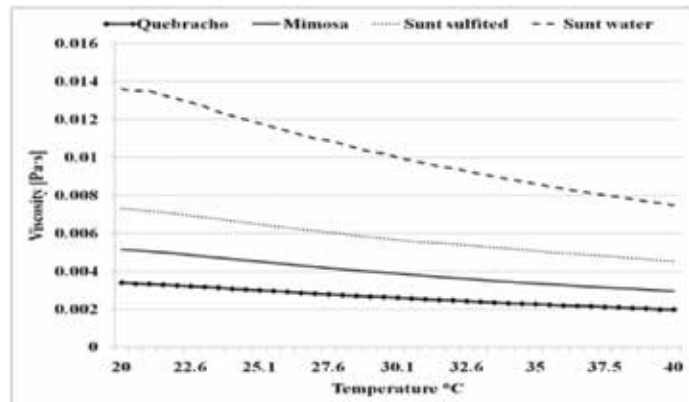


Figure 2. Viscosity of 20% concentration from different extracts.

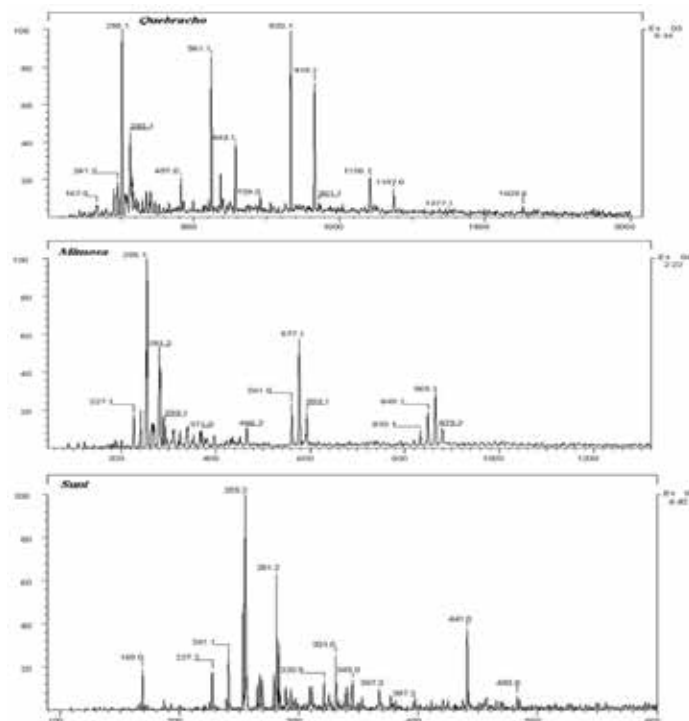


Figure 3. Mass spectrum for different extracts.

In the present study, the spectrum of sunt pods extract showed a foundation for condensed and hydrolysable tannins. The peak at  $M= 442$  Da indicates the epicatechin-gallate compound which is considered galloyl-esterification of procyanidins. On the other hand, peaks at  $M= 170, 322, 332$  and  $484$  corresponded to gallic acid, m-digallic, monogalloyl-glucose and digalloyl-glucose, respectively, which indicates the presence of gallotannins as a type of hydrolysable tannins.

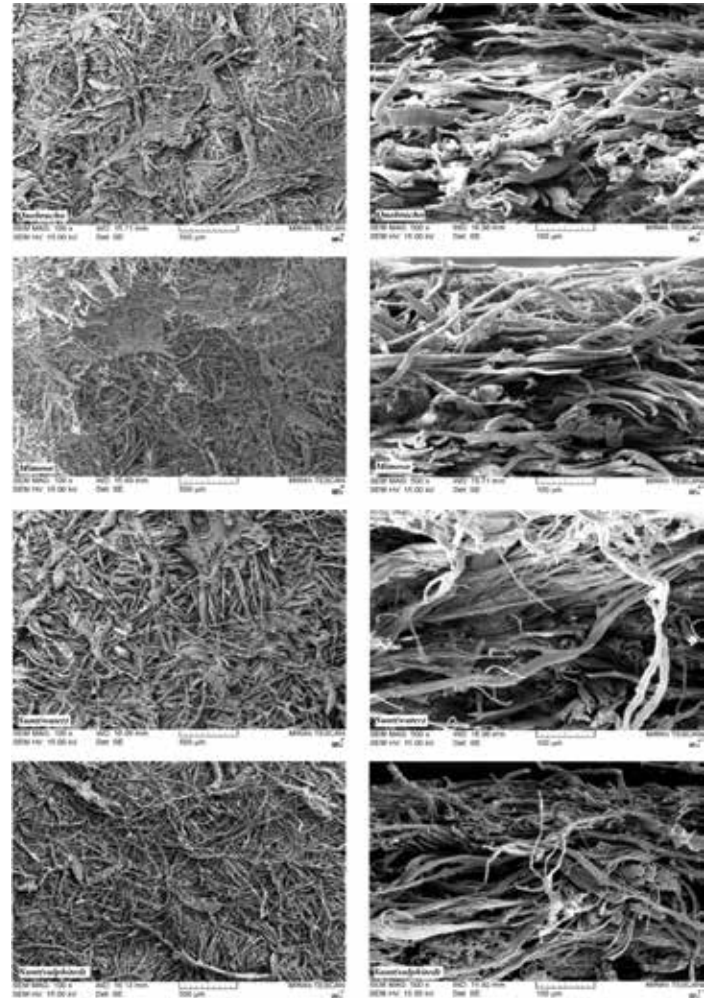


Figure 4. Electron micrographs of vegetable tanned leathers.

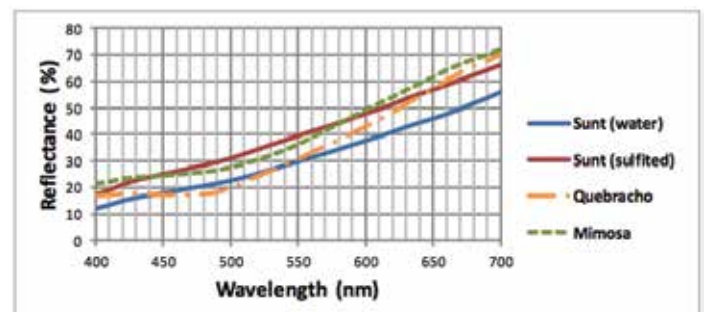


Figure 5. Reflectance spectra for crust leather.

**Table III**  
Least Square Means  $\pm$  SEM of Leather Physical Properties.

Item	Quebracho	Mimosa	Sunt		SEM	Significant	
			Water	Sulfited			
Thickness (mm)	0.84	0.94	0.95	0.91	0.02	NS	
Density (g/cm <sup>3</sup> )	0.59	0.62	0.59	0.62	0.01	NS	
Tensile Strength (kg/cm <sup>2</sup> )	188.21 <sup>a</sup>	114.29 <sup>b</sup>	182.31 <sup>a</sup>	157.35 <sup>ab</sup>	10.54	*	
Elongation (%)	34.14 <sup>b</sup>	38.88 <sup>b</sup>	50.45 <sup>a</sup>	45.02 <sup>a</sup>	1.82	**	
Tear Strength (kg/cm)	9.94 <sup>b</sup>	11.98 <sup>b</sup>	13.45 <sup>ab</sup>	16.99 <sup>a</sup>	0.95	*	
PWV (mg/cm <sup>2</sup> /hr.)	1.94	1.87	1.79	1.77	0.03	NS	
Water Abs. (%)	2h	163.00 <sup>a</sup>	131.43 <sup>b</sup>	154.40 <sup>a</sup>	150.87 <sup>a</sup>	3.67	**
	24h	169.40	147.70	159.47	161.26	3.95	NS
Shrinkage Temp. (°C)	70.98 <sup>a</sup>	73.79 <sup>a</sup>	67.74 <sup>b</sup>	65.08 <sup>b</sup>	0.95	**	
Color	Reddish Brown	Pale Reddish Brown	Dark Beige	Beige	--	--	

<sup>a, b</sup>Means in the same row having different superscript letters are significantly different ( $P < 0.05$ ).

\*Significant at  $P < 0.05$ .

\*\*Highly significant at  $P < 0.01$ .

NS Not Significant.

PWV = Permeability to water vapor.

**Table IV**  
Least square means  $\pm$  SEM of leather chemical properties.

Group	%						pH
	Moisture	Ash	Fat	Soluble Matter	Hide Substance	Tanning Degree	
Quebracho	15.62 <sup>a</sup>	0.49 <sup>a</sup>	5.76	0.94 <sup>b</sup>	50.44	56.46	4.96 <sup>a</sup>
Mimosa	14.38 <sup>b</sup>	0.47 <sup>ab</sup>	6.89	0.87 <sup>b</sup>	49.93	55.15	4.35 <sup>c</sup>
Sunt (water)	11.93 <sup>d</sup>	0.50 <sup>a</sup>	5.60	1.42 <sup>a</sup>	49.18	63.82	4.33 <sup>c</sup>
Sunt (sulfited)	13.65 <sup>c</sup>	0.45 <sup>b</sup>	6.08	1.00 <sup>b</sup>	51.10	54.88	4.67 <sup>b</sup>
SEM	0.35	0.01	0.33	0.07	0.61	2.06	0.07
Significance	**	*	NS	**	NS	NS	**

<sup>a, b, c, d</sup>Means in the same column having different superscript letters are significantly different ( $P < 0.05$ ).

\*Significant at  $P < 0.05$

\*\*Highly significant at  $P < 0.01$

NS Not Significant

**Table V**  
CIE L\*a\*b\* data of the crust leathers.

D65/10°	Sunt (water)	Sunt (sulfited)	Quebracho	Mimosa
L*	61.9	69.3	63.3	68.1
a*	8.7	7.4	15.5	13.3
b*	21.2	20.7	24.7	19.5

### Leather Properties

In the current work, both water sunt pods and sulfited sunt pods extracts are considered the best extracts based on results of extracts characteristics. Thus, scanning electron micrographs of the tanned leathers (Figure 4) show that collagen fibers in leathers tanned with quebracho and mimosa extracts were more cemented and finer than those tanned with water and sulfited sunt extracts. Furthermore, leathers tanned with water sunt extract had more cemented and swelled fibers than leathers tanned with sulfited sunt extract. In the meantime, even though quebracho and mimosa tanned leathers are superior over sunt tanned leathers regarding collagen fibers shapes, there was less difference in physical and chemical properties. The least square means and SEM of physical and chemical properties are presented in tables III and IV, respectively. Leather thickness, density, permeability to water vapor and water absorption values did not significantly differ among all tanned leathers. This gave an indication to the similarity among all extracts in the fullness effect with collagen fibers.

Within tensile strength values, mimosa tanned leathers recorded the lowest value (114.29 kg/cm<sup>2</sup>), while other tanned leathers showed no significant difference. With respect to tearing strength and elongation properties, sunt tanned leathers were higher values than corresponding values in quebracho and mimosa tanned leathers. On the other hand, shrinkage temperature values for tanned leathers ranged from 65 to 75°C but sunt tanned leather values were lower than for quebracho and mimosa tanned leathers.

The main purpose for determining the moisture, ash, fat, soluble matter and hide substance is to calculate tanning degree, which did not differ among all tanned leathers. While pH values differed significantly, the range seemed narrow (pH 4.33 to 4.96). Therefore, the recommended tanning degree and pH values of light vegetable tanned leather should exceed 50% and 3.5 respectively,<sup>37</sup> which was surpassed by all tanned leathers.

By comparing the physical and chemical properties of all tanned leathers obtained from this study with an acceptable limitation range for light vegetable tanned leathers,<sup>37</sup> it can be concluded that sunt pods extracts can be used successfully in leather tanning in addition to quebracho and mimosa extracts.

Vis reflectance spectra of the crust leather show that the curves of sunt tanned leather increased in a more linear fashion and that these curves are not very different than those of water and sulfited extract. The curves of quebracho and mimosa tanned leather show an approximately constant level of 17-27% reflectance from 400 nm to 500 nm, then increase to nearly 70% at 700 nm. The sunt leather is more yellow than the quebracho and mimosa leather with a red cast (Table V).

### Conclusions

The results of the current work clarified that sunt pods contain both condensed and hydrolysable tannins, which can be utilized in the leather tanning industry in a level comparable to quebracho and mimosa extracts. Moreover, increasing extraction temperature from 70°C to 90°C not only increased the extraction yield, but also improved the quality of extracts in certain criteria; such as the number of tannins, the tannins to non-tannins ratio, hide powder and stiasny number. The results also demonstrated that either extractions with a 2.5% Na<sub>2</sub>SO<sub>3</sub> aqueous solution at 90°C or water extraction at the same high temperature resulted in similar high quality extracts from sunt pods. However, the optimizations of the extraction process, as well as the effect of increasing the extracting temperature above 90°C, and using different drying methods still need to be addressed.

### Acknowledgment

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### References

1. Elgailani, I. H. and Ishak, C. Y.; Determination of Tannins of Three Common Acacia Species of Sudan. *Advances in Chemistry* 2014, 1-5, 2014.
2. Heidemann, E.; Fundamentals of leather manufacture. Eduard Roether KG Druckerei und Verlag, Darmstadt, Germany, 1993.
3. Zaghlol, M. A.; Leathers, types, preparation, tanning and finishing. Press in Arabic, Egyptian Anglo Publishing, Egypt, 1962.

4. Gledhill, D.; The names of plants. 4<sup>th</sup> ed., Cambridge University Press, UK, 2008.
5. Elkhalfifa, K. F., Suliman, I. and Assubki, H.; Variations in tannin's contents of *Acacia nilotica* (L.) Willd. ex Del. in the Sudan. *Pakistan J. of Biological Sci.* **8**, 1021-1024, 2005.
6. Margaret Theresa, Y. and Nayudamma, Y.; A comparative study of Babul pod tannins of India (*Acacia arabica*) and Sudanese (*Acacia nilotica*) origin. *Leather Sci.* **19**, 341-348, 1972.
7. Sarkar, K. T.; Theory and practice of leather manufacture. 2<sup>nd</sup> ed., C.L.S. Press, Madras, 1991.
8. El-Sissi, H.I., El Sherbeiny, A. E. A. and Saleh, N. A. M.; Local plants as potential sources of tannins *Acacia nilotica*. *Plant Foods for Human Nutrition* **12**, 390-396, 1965.
9. Ahmed, M., Khirstova, P. and Icho, G.; Comparative study of tannins of *Acacia nilotica* an indigenous tanning material in Sudan with *Acacia mearnsii*. *Suranaree J. Sci. Technol.* **12**, 259-265, 2005.
10. Voulgaridis, E.; Grigoriou, A. and Passialis, C.; Investigations on bark extractives of *Pinus halepensis* mill. *Holz als Roh- und Werkstoff.* **43**, 269-272, 1985.
11. Galvez, J. M., Riedl, B. and Conner, A. H.; Analytical studies on Tara tannins. *Holzforschung* **51**, 235-243, 1997.
12. Li, J. and Maplesden, F.; Commercial production of tannins from radiata pine bark for wood adhesives, *IPENZ Transactions* **25**, 46-52, 1998.
13. Vázquez, G., González-Alvarez, J., Santos, J., Freire, M. S. and Antorrena, G.; Evaluation of potential applications for chestnut (*Castanea sativa*) shell and eucalyptus (*Eucalyptus globulus*) bark extracts. *Industrial crops and products* **29**, 364-370, 2008.
14. Hoong, Y., Paridah, B. M. T., Luqman, C. A., Koh, M. P. and Loh, Y. F.; Fortification of sulphited tannin from the bark of *Acacia mangium* with phenol-formaldehyde for use as plywood adhesive. *Industrial Crops and Products* **30**, 416-421, 2009.
15. Binko, I. and Kolar, J.; Extracting tanning agent with cation containing solution with subsequent cation exchange. U.S. Patent 2,934,398, patented Apr. 26, 1960.
16. Roux, D. G., Ferreira, D., Hundt, H. K. L., Malan E.; Structure, stereochemistry and reactivity of natural condensed tannins as basis for their extended industrial application. *Applied Polymer Symposium* **28**, 335-353, 1975.
17. Anonymous, *Quantification of tannins in tree foliage*. FAO/IAEA Working Document, Vienna, 2000.
18. American Society for Testing and Materials, Soaps and Other Detergents, Polishes, Leather, Resilient Floor Coverings. Annual Books of ASTM Standards vol. 15.04, 2013.
19. Rama Devi, S. and Prasad, M. N. V.; Tannins and related polyphenols from ten common *Acacia* species of India. *Bioresource Technol.* **36**, 189-192, 1991.
20. Mahdi, A., Palmina, K. and Glavtch, I.; Characterization of *Acacia nilotica* as an indigenous tanning material of Sudan. *J. of Tropical Forest Sci.* **18**, 181-187, 2006.
21. Faber, K.; Bibliothek des Leders. Band 3 Gerbmittel, Gerbung, Nachgerbung, Umschau Verlag, Frankfurt am Main, Germany, 2<sup>nd</sup> ed., pp. 32-38, 1990.
22. Beg, M. A. and Siddiqui, Z. A.; Infrared Spectroscopic Investigation of Tannins. *Die Angewandte Makromolekulare Chemie* **7**, 67-78, 1969.
23. Ibrahim, M. N. M., Nor Nadiah, M. Y. and Amirue, A. A.; Extraction of tannin from oil palm empty fruit bunch as a rust deactivator. *Materials Sci. and Engineering, Regional symposium on chemical engineering* (Hanoi, Vietnam), 2005.
24. Lee, W. and Lan, W.; Properties of resorcinol-tannin-formaldehyde copolymer resins prepared from the bark extracts of Taiwan *Acacia* and China fir, *Bioresource Technol.* **97**, 257-264, 2006.
25. Diab, M. A.; Separation and characterization of lignin obtained from kraft pulping black liquor of ligno cellulosic materials. MSc. Thesis, Faculty of Sci., Alex. Univ., 2007.
26. Nakamoto, Y., Tsunoda, T., Ono, K., Kageyama, N., Yazaki, Y., Jiang, H., Lawson, F. and Theodore, P. H.; US Pat., 0054055, 20 March 2003.
27. Barry, K. M.; Davies, N. W. and Mohammed, C. L.; Identification of hydrolysable tannins in the reaction zone of eucalyptus nitens wood by high performance liquid chromatography- electrospray ionisation mass spectrometry. *Phytochem. Anal.* **12**, 120-127, 2001.
28. Roesler, R., Catharino, R. R., Malta, L. G., Eberlin, M. N. and Pastore, G.; Antioxidant activity of *Annona crassiflora*: Characterization of major components by electrospray ionization mass spectrometry. *Food Chem.* **104**, 1048-1054, 2007.
29. Streit, W. and Fengel, D.; Purified tannins from Quebracho Colorado. *Phytochemistry* **36**, 481-482, 1993.
30. Pasch, H., Pizzi, A. and Rode, K.; MALDI-TOF mass spectrometry of polyflavonoid tannins. *Polymer* **42**, 7531-7539, 2001.
31. Kardel, M., Taube, F., Schulz, H., Schütze, W. and Gierus, M.; Different approaches to evaluate tannin content and structure of selected plant extracts – review and new aspects. *J. of Applied Botany and Food Quality* **86**, 154-166 2013.

- 
32. Jordaan, M. A.; The analysis of natural and sulfited commercial quebracho (*Schinopsis lorentzii*) and Acacia (*Acacia mearnsii*) proanthocyanidin extracts with electrospray ionisation mass spectrometry, PhD Thesis, Faculty of Nat. and Agri. Sci., Univ. of the Free State Bloemfontein, 2013.
  33. El Sissi, H. I. and El Sherbeiny, A. E. A.; Local plants as potential sources of tannins in Egypt, part III. *Plant Foods for Human Nutrition* **14**, 28-36, 1967.
  34. Malan, E.; Derivatives of (+)-catechin-5-gallate from the bark of *Acacia nilotica*, *Photochemistry* **30**, 2723-2739, 1991.
  35. Dube, J.S., Reed, J.D. and Ndlovu, L.R.; Proanthocyanidins and other phenolics in Acacia leaves of Southern Africa. *Animal Feed Sci. and Technol.* **91**, 59-67, 2001.
  36. Sundaram, R. and Mitra, S. K.; Antioxidant activity of ethyl acetate soluble fraction of *Acacia arabica* bark in rats. *Indian J. Pharmacol.* **39**, 33-38, 2007.
  37. Anonymous, *Pocket book for leather technologist*. BASF, Aktiengesellschaft, Germany, 2007.
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