

## THE MECHANICAL AND PHYSICAL PROPERTIES OF LEATHER TANNED BY VEGETABLE TANNIN: A META-ANALYSIS STUDY

### SIFAT MEKANIK DAN FISIK KULIT YANG DISAMAK DENGAN TANIN NABATI: SEBUAH KAJIAN META-ANALISIS

Aditya Wahyu Nugraha<sup>1)\*</sup>, Amalia Afifah<sup>1)</sup>, Borneo Satria Pratama<sup>2)</sup>, Anuraga Jayanegara<sup>3)</sup>

<sup>1)</sup>Department of Agroindustrial Technology, Institut Teknologi Sumatera,  
Jalan Terusan Ryacudu, Way Hui, Jati Agung, South Lampung 35365, Indonesia

<sup>2)</sup>Department of Agricultural Technology, Politeknik Negeri Pontianak, Pontianak, West Kalimantan, Indonesia

<sup>3)</sup>Department of Nutrition and Feed Technology, Faculty of Animal Science, IPB University, Bogor 16680, Indonesia  
Email: [aditya.wahyu28@gmail.com](mailto:aditya.wahyu28@gmail.com)

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#### ABSTRAK

Penyamakan nabati merupakan cara yang menjanjikan untuk mengurangi atau menghilangkan penggunaan krom yang dimanfaatkan dalam proses penyamakan kulit konvensional. Metode penyamakan nabati telah banyak diterapkan dengan memanfaatkan beragam tanin yang berasal dari tumbuhan. Namun, kajian komprehensif yang membandingkan pengaruh berbagai jenis tanin nabati terhadap karakteristik kulit tersamak masih terbatas. Penelitian ini bertujuan untuk mengevaluasi pengaruh penyamakan nabati terhadap sifat fisik dan mekanik kulit berdasarkan tinjauan literatur ilmiah. Studi ini menggunakan meta-analisis, sebanyak tiga belas artikel ilmiah yang memenuhi kriteria inklusi dianalisis dalam penelitian ini. Ukuran efek dihitung menggunakan Hedges' *d*, dan model efek acak diterapkan untuk mengintegrasikan temuan dari berbagai studi. Potensi bias pada publikasi dievaluasi melalui funnel plot. Hasil meta-analisis menunjukkan bahwa penyamakan nabati tidak menghasilkan perbedaan signifikan shrinkage temperature, tensile strength, tear strength, atau elongation at break ( $p > 0.05$ ). Meskipun demikian, jenis tanaman yang menjadi sumber tanin terbukti berpengaruh penting terhadap sifat fisik dan mekanik kulit. Sebaliknya, jenis kulit maupun spesies hewan tidak memberikan pengaruh yang berarti. Secara keseluruhan, variasi karakteristik kulit terutama ditentukan oleh jenis tanin yang terkandung dalam bahan nabati yang digunakan pada proses penyamakan.

Kata kunci: meta-analysis, keberlanjutan, penyamakan, tanin nabati

#### ABSTRACT

Vegetable tanning is a promising technique to cut down on or get rid of chromium in traditional leather processing. It has already been used with a wide range of plant-based tannins. Even with this advancement, there aren't many systematic comparisons of how different vegetable tannins affect the quality of leather. This study aimed to assess the impact of vegetable tanning on essential physical and mechanical qualities of leather, utilizing data from thirteen peer-reviewed publications to fill this gap. This study performed a meta-analysis, Hedges' *d* was used to figure the effect sizes, and a random-effects model was used to put together results from several trials. Funnel plots were utilized to investigate potential publication bias. The meta-analysis showed that there were no big changes in shrinkage temperature, tensile strength, rip strength, or elongation at break ( $p > 0.05$ ). However, certain plant sources were identified as significant contributors to the physical and mechanical properties of the resultant leather. On the other hand, the type of skin or the animal species did not have a big effect on the qualities of the leather. In general, the results reveal that the exact combination of tannins in the plant materials used for vegetable tanning has the largest effect on how leather works.

Keywords: meta-analysis, sustainability, tanning, vegetable tannin

#### INTRODUCTION

Tanning is one of the oldest technological processes that people have used. It turns raw hides and skins into strong leather that is less likely to break down. Despite its long history, the tanning process creates a lot of solid and liquid waste at different points in the production process. Nugraha *et al.* (2018) stated that processing 1.5 tons of salted hides can produce up to 29.3 m<sup>3</sup> of liquid waste and 1.75 tons (wet basis) of solid waste per batch. Bhargavi *et*

*al.* (2015) and Sekaran *et al.* (2007) noted that the tanning of 1 kg of skin produces 30–35 liters of liquid effluent and approximately 0.7 kg of solid waste. Tanning is a crucial process that alters the physical, chemical, and mechanical characteristics of the final leather. During this process, tanning chemicals engage with collagen fibers in the skin, generating covalent, hydrogen, or coordination interactions (Covington *et al.*, 2019). In the past, chromium sulfate has been the most popular tanning chemical because it makes leather that is more heat-resistant,

stronger, and less likely to tear. But the effects of chromium-based tanning on the environment have become a major problem.

For hundreds of years, people have been worried about the health and environmental effects of tanning. This is partly because the strong smells that came from early tanneries when fleshings, liming solutions, and other byproducts started to break down. Scientific investigations into these subjects intensified in the late nineteenth and early twentieth centuries. By the late 1980s, environmental scrutiny intensified regarding the hazards associated with various chemical additives, including surfactants, alongside increasing evidence of the carcinogenic risks linked to hexavalent chromium (Palumbo *et al.*, 2020).

Chromium is known to cause cancer. Chromium levels in leather tanning wastewater have been shown to range from 3 to 350 mg/L (Midha *et al.*, 2008), and about 40% of the chromium salts used in processing are released directly into the effluent (Chowdury *et al.*, 2013). These levels are much higher than the 0.6 mg/L limit set by the Indonesian Ministry of Environment and Forestry (2014). The oxidation of trivalent chromium ( $\text{Cr}^{3+}$ ) into its more dangerous hexavalent form ( $\text{Cr}^{6+}$ ) makes the situation worse by making the environment and health risks higher (Prado *et al.*, 2016). Hexavalent chromium is extremely dangerous; it is about 100 times more toxic than  $\text{Cr}^{3+}$  (Tegtmeier, 2013), and its accumulation in the body can lead to cancer, mutations, and birth defects (Costa *et al.*, 2006; Ashraaf *et al.*, 2017). Evidence shows that wastewater from tanning can carry about 0.62 mg/L of  $\text{Cr}^{6+}$ , re-tanning wastewater can reach roughly 2.09 mg/L, and water coming out of treatment plants can still contain around 0.03 mg/L. This illustrates how much  $\text{Cr}^{6+}$  is created when leather is tanned.

To meet Sustainable Development Goals 12 (Responsible Consumption and Production) and 6 (Clean Water and Sanitation), we need to cut down on the primary environmental effects of making leather, namely the high levels of chromium in wastewater and the inefficient use of water. These issues can be lessened by improving processes and employing modern technologies (Chiampo *et al.*, 2023). Businesses are encouraged to have less of an effect on the environment in line with the principles of sustainable development. This makes the quest for eco-friendly tanning options even more crucial (Emiliana *et al.*, 2021). Using vegetable tannins is one technique to make chromium less harmful. These tannins are naturally occurring polyphenolic compounds found in plants that usually attach to collagen fibers by hydrogen bonding. This alters the leather's physical, chemical, and mechanical characteristics (Mustafa *et al.*, 2024). Mimosa is a plant-based tanning agent that is widely used to manufacture leather that shrinks at roughly 80°C (Missio *et al.*, 2017). Vegetable-tanned leather

doesn't operate the same way as chrome-tanned leather, but it does assist with pollution and cut down on chromium waste.

In addition to mimosa, several other plants can also serve as sources of vegetable tannins, such as *Acacia mearnsii*, *Potentilla erecta* (L.) Raeusch, *Trema orientalis* (L.), *Ceriops tagal*, areca nut, *Schinopsis lorentzii*, *Cassia fistula*, *Pinus roxburghii*, *Maclura cochinchinensis*, *Azadirachta indica*, *Acacia nilotica*, *Terminalia chebula*, *Uncaria gambir*, *Castanea sativa*, and *Caesalpinia spinosa*. The tannins in each of these plants are made up of different things and have varied intensities. These natural differences can affect the physical and mechanical properties of the leather made from them. There has been a lot of research on vegetable tanning, however there aren't enough detailed comparisons of different plant-based tanning chemicals. Comparisons like this are quite helpful for finding the best and most environmentally friendly alternatives to traditional ways. A meta-analysis is a comprehensive method for integrating current data and discerning overall trends. The goal of this study was to look at several vegetable tanning chemicals used in leather processing and observe how each one changes the leather's properties.

## MATERIAL AND METHODS

### Database Development

The data for this study were derived from several published sources, including journal articles, mini-theses, theses, and dissertations. The study selection was exclusively concentrated on research examining leather tanning procedures utilizing vegetable tannin-based ingredients. We used well-known databases like Scopus, Elsevier, Google Scholar, and ResearchGate to find articles that were useful. We also used certain publications from the Leather and Footwear Journal, the Journal of the American Leather Chemists Association, and relevant university theses as sources. We looked through the literature for the words "vegetable tanning," "leather," and "tanning." Figure 1 is a flowchart that explains how to pick studies to use to make a database.

To ensure the credibility of the results, the evaluation strictly incorporated research utilizing only vegetable tannins devoid of synthetic additions, employing mimosa tannin as the control. The exclusion criteria were: (1) the utilization of mineral tanning agents or their combinations, and (2) vegetable tanning research lacking mimosa as a control. We took the mean values, standard deviations, and sample sizes for both the treatment and control groups from each study that qualified. Table 1 shows a summary of all the studies that were part of the meta-analysis. This meta-analysis concentrated on four principal outcomes: shrinkage temperature, tensile strength, rip strength, and elongation at break.

Table 1. Description of studies used in the meta-analysis

Plant and Tannin source	Animal Type	Shrinkage temperature	Tensile strength	Tear strength	Elongation at break	Source
<i>Acacia nilotica</i> (bark), <i>Acacia xanthophloea</i> (bark), <i>Hagenia abyssinica</i> (bark)	Sheep	V	V	V	X	(Kuria <i>et al.</i> , 2016)
<i>Ceriops tagal</i> (bark)	Fish	X	V	V	V	(Kasmudjiastuti <i>et al.</i> , 2019)
<i>Plectranthus barbatus</i> (leaf, stem and both combination)	Goat	V	V	V	V	(Obiero <i>et al.</i> , 2020)
Quebracho (bark)	Sheep	X	V	V	V	(Nasr <i>et al.</i> , 2017)
Quebracho (bark)	Calf	X	X	X	X	(Omur <i>et al.</i> , 2016)
<i>Castanea spp.</i> / Chestnut (bark), Quebracho (bark)	Sheep and Calf	V	X	X	X	(Carsote <i>et al.</i> , 2016)
<i>Acacia nilotica</i> (sunt pod), quebracho (bark)	Sheep	V	V	V	V	(Nasr <i>et al.</i> , 2017)
<i>Rumex abyssinicus</i> (root)	Goat	V	V	V	V	(Mohammed <i>et al.</i> , 2020)
Cashew fruits (husk)	Goat	V	V	V	V	(Ukoha <i>et al.</i> , 2010)
<i>Acacia nilotica</i> (bark), Pomegranate (husk), Mango (leaf), Quebracho (bark)	Sheep	V	V	V	V	(Moursi, 2011)
Sodom apple/ <i>Solanum incanum</i> (fruit)	Goat	V	V	V	V	(Badessa <i>et al.</i> , 2022)
<i>Lawsonia inermis</i> (leaf), <i>Emblica officinalis</i> (fruit)	Buffalo	X	V	X	X	(Senarane <i>et al.</i> , 2015)
<i>H. abyssinica</i> (bark)	Sheep	V	V	V	V	(Unango <i>et al.</i> , 2021)
Total Articles		9	11	10	9	

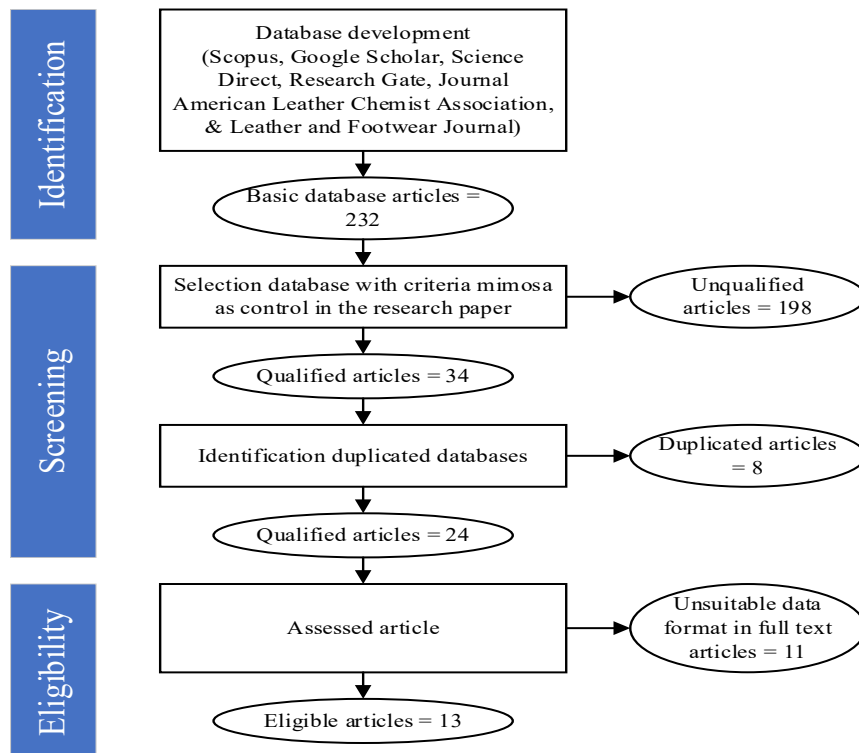


Figure 1. Detail of the study selection process

**Data Analysis**

We put the data into Microsoft Excel and then looked at it with OpenMEE, an open-source program made just for meta-analysis. We used Hedges' d to find the effect size (d) as a standardized mean difference, as shown in Equation 1 (Rosenberg *et al.*, 2000; Sánchez-Meca and Marín-Martínez, 2010; Palupi *et al.*, 2012).

$$d = \frac{(x^e - x^c)}{s} J \dots\dots\dots (1)$$

In Equation 1,  $X^e$  is the mean of the experimental group,  $X^c$  is the mean of the control group,  $s$  is the pooled standard deviation, and  $J$  is the correction factor for small sample sizes. Equation 2 shows how to write the one-way random-effects model in math.

$$y_i = \theta + v_i + \varepsilon_i \dots\dots\dots (2)$$

In Equation 2,  $Y_i$  stands for the effect size (Hedges' d),  $\theta_i$  stands for the true effect for the  $i$ -th study,  $v_i$  stands for the true variance of the effect size, and  $\varepsilon_i$  stands for the error term that goes with it. We used the DerSimonian and Laird method, which is shown in Equation 3, to find the between-study variance ( $\tau^2$ ). In this equation,  $Q$  stands for the weighted sum of squares,  $df$  stands for the degrees of freedom, and  $C$  stands for a constant value (DerSimonian *et al.*, 1986).

$$\tau^2 = \frac{Q - df}{c} \dots\dots\dots (3)$$

**RESULTS AND DISCUSSION**

**Shrinkage Temperature**

The use of non-mimosa vegetable tannins did not lead to a statistically significant change in shrinkage temperature compared to the control, which employed mimosa tannin. Table 2 shows a p-value of 0.176, which is higher than 0.05. This means that there is no significant difference. Figure 2 shows that in 15 of the 21 studies, the control group had higher shrinkage temperatures than the experimental treatments. In six studies, on the other hand, the opposite was true, showing that alternative tannins made a big difference.

The meta-analysis in Table 2 demonstrates that the studies are not very similar to each other. A significant  $Q$  value ( $Q = 108.58$ ;  $p < 0.001$ ), a  $\tau^2$  of 6.47, and an  $I^2$  of 86.19% demonstrate this. The substantial variability noted indicates that the primary variation in effect sizes stems from differences in study variables rather than random error. The random-effects model gave us a pooled effect size of  $-1.217$  (95% CI:  $-2.745$  to  $0.311$ ), which suggests that the temperature at which the material shrinks is likely to go down. But the confidence interval contains zero, which suggests that the overall effect is not statistically significant.

Table 2. Cumulative effect size (d++) with 95% confidence intervals (CI) for the influence of vegetable tanning materials on shrinkage temperature across subgroups: (a) plant species, (b) animal species, and (c) hide/skin type.

Subgroup	Category	Estimate	Lower Bound	Upper Bound	Std. Error	p-Val
Plant type	<i>Acacia nilotica</i>	-1.388	-2.358	-0.418	0.495	0.005*
	Chestnut	-4.569	-8.408	-0.730	1.959	0.020*
	<i>Acacia xanthophloea</i>	3.781	2.145	5.417	0.835	NA
	<i>Rumex abyssinicus</i>	-1.009	-2.708	0.690	0.867	NA
	<i>Hagenia abyssinica</i>	-5.672	-7.868	-3.476	1.120	NA
	Mango	-1.802	-3.446	-0.159	0.838	NA
	<i>Plectranthus barbatus</i>	-104.932	-147.945	-61.919	21.946	< 0.001*
	Mango	-1.802	-3.446	-0.159	0.838	NA
	Quebracho	-0.111	-2.398	2.175	1.167	0.924
	Pomegranate	0.046	-1.340	1.432	0.707	NA
	Cashew fruits	15.061	7.879	22.243	3.665	< 0.001*
	Sodom apple	-9.389	-14.937	-3.841	2.831	NA
	Sheep	-0.928	-2.214	0.357	0.656	0.157
	Animal type	Calf	-2.375	-7.633	2.883	2.683
Goat		-2.095	-13.392	9.202	5.764	0.716
Skin		-0.735	-2.214	0.744	0.754	0.330
Hide / Skin	Hide	-2.375	-7.633	2.883	2.683	0.376
	Overall	-0.966	-2.365	0.434	0.714	0.176

Note: \*:Significant; NA: not analyzed

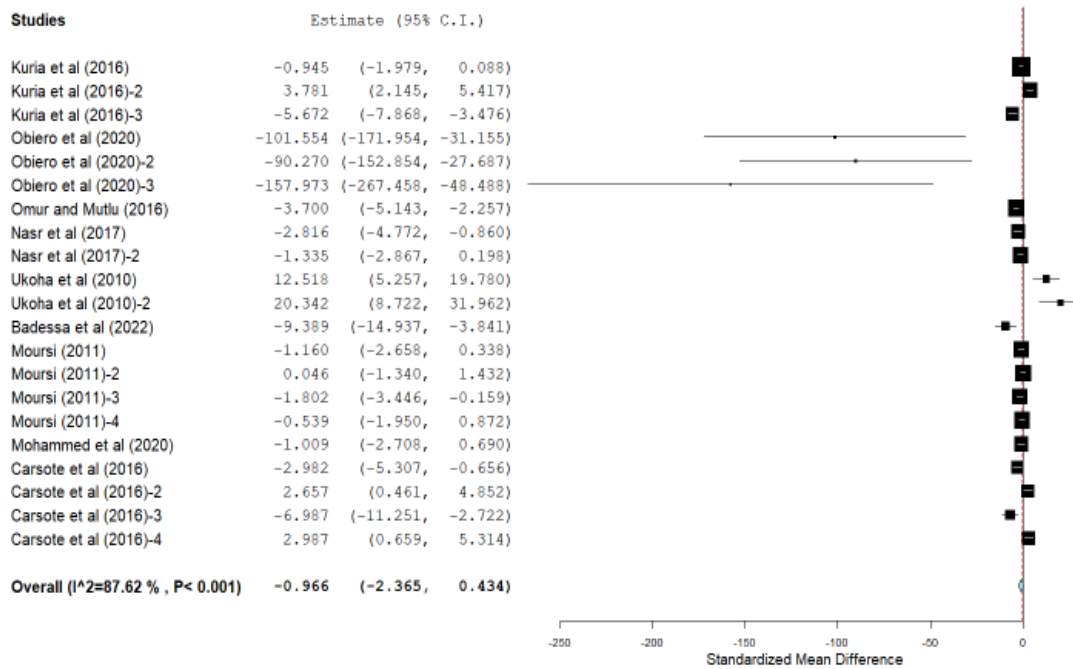


Figure 2. Forest plot of the cumulative effect size (d++) with 95% confidence intervals (CI) for the influence of vegetable tanning agents on shrinkage temperature

The leave-one-out strategy for sensitivity analysis demonstrated that no individual study altered the direction of the pooled effect. Several experiments with very large effect sizes, especially those involving *Plectranthus barbatus*, had an effect on  $\tau^2$  and the size of the pooled estimate. This means that these were important research. The results show that the meta-analytic findings are mostly trustworthy.

The subgroup analysis covered 11 plant sources, including *Hagenia abyssinica*, *Rumex abyssinicus*, cashew fruits, *Acacia xanthophloea*, chestnut, mango, *Plectranthus barbatus*, pomegranate, *Acacia nilotica*, *Quebracho*, and Sodom apple. Four tannin sources—chestnut, cashew fruits, *Plectranthus barbatus*, and *Acacia nilotica*—demonstrated considerably greater effects compared to the control ( $p < 0.05$ ) (Table 2). The cashew fruits had the biggest effect on shrinking temperature of all the sources tested, with a value of 15.061, which was better than the mimosa control.

*Acacia nilotica* had an effect size of  $-1.388$ , *Plectranthus barbatus* showed an effect size of  $-104.932$ , and chestnut recorded an effect size of  $-4.569$ . These numbers show that the temperatures at which these tannins shrink were lower than those of the mimosa control. Figure 3a shows that different plant-based tannins caused big changes in shrinkage temperature, with some going up and some going down compared to the control. Because the sample sizes for each plant species were small, statistical significance tests were not done (Table 2). The data in Table 2 show that the choice of vegetable tanning agent did not have a big effect on shrinkage temperature, no matter what kind of animal or hide/skin it was from. Figures 3b and 3c show that

mimosa tannin usually makes things shrink at higher temperatures than non-mimosa vegetable tannins, especially when it comes to sheep, goat, and calf hides and skins.

The examination of animal species and hide/skin types in Table 2 demonstrates that the use of different vegetable tanning agents did not significantly influence the shrinkage temperature of the resultant leather. Figures 3b and 3c show that mimosa tannin usually makes the hides and skins of sheep, goats, and calves shrinkage temperatures than other vegetable tanning agents. Shrinkage temperature is an important factor for testing thermal stability because it shows how strong the interactions are between tanning agents and collagen fibers. Tannins, which are naturally occurring polyphenolic compounds, form hydrogen bonds with reactive groups in collagen during vegetable tanning (Ucar *et al.*, 2013; Bharudin *et al.*, 2013; Duki *et al.*, 2013). When leather contact with high temperature, this process makes it more stable. Sebestyen *et al.* (2019) said that tannins can be hydrolyzable, condensed, or complicated. This is why vegetable-tanned leathers shrink at high temperatures. Carsote *et al.* (2016) and Sebestyen *et al.* (2019) assert that condensed tannins generally demonstrate elevated shrinkage temperatures relative to other tannin classifications, owing to the existence of two dihydroxybenzene ring topologies rich in hydrogen-bonding sites. These structural traits let condensed tannins connect with collagen fibers in a stronger way. Badea *et al.* (2016) noted that, in addition to hydrogen bonding, the establishment of covalent bonds further improves the thermal stability of leather tanned with condensed tannins.

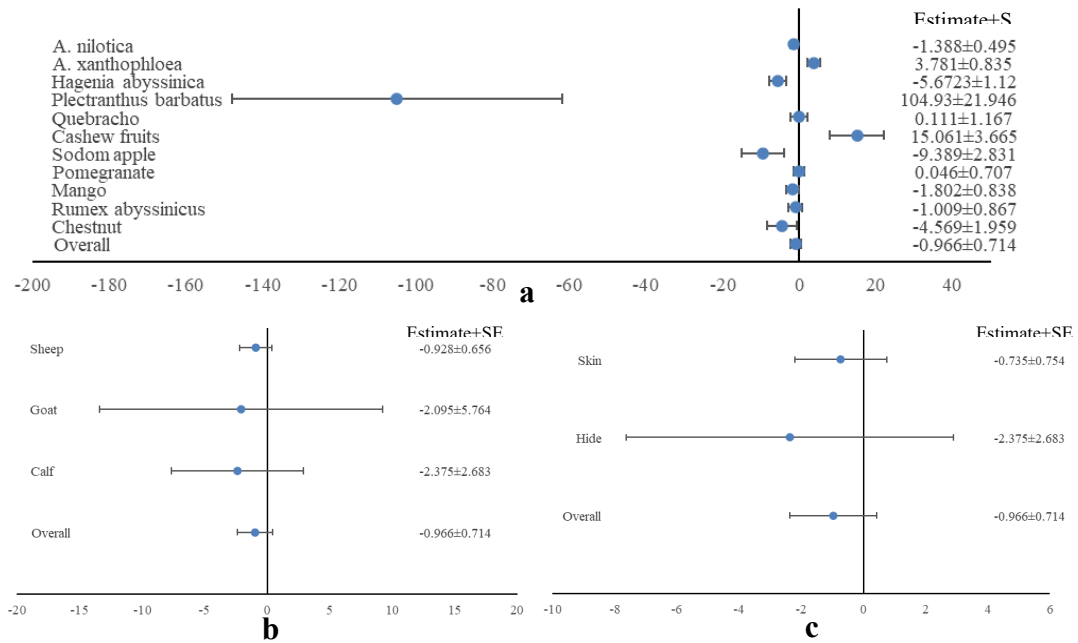


Figure 3. Forest plot of the cumulative effect size ( $d^{++}$ ) with 95% confidence intervals (CI) for the influence of vegetable tanning materials on shrinkage temperature across subgroups: (a) plant species, (b) animal species, and (c) hide/skin type

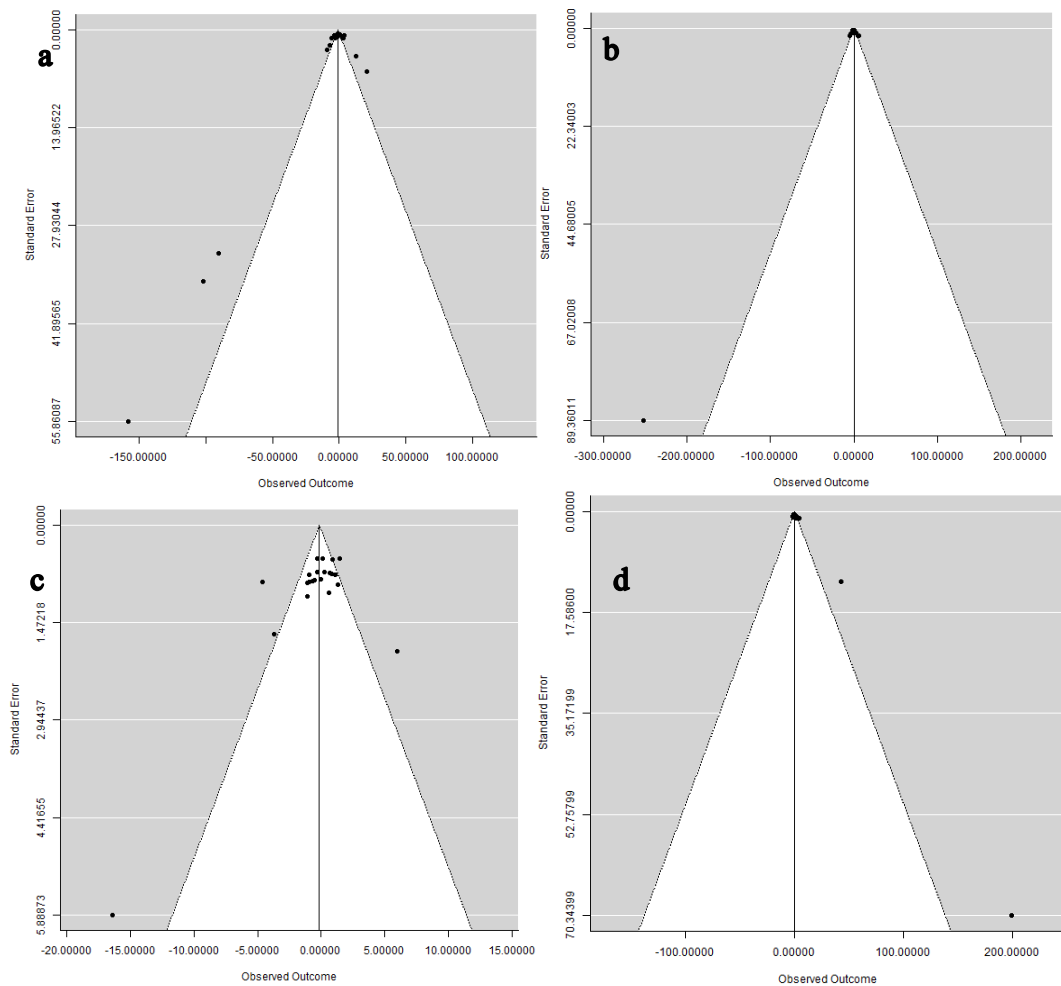


Figure 4. Funnel plots for: (a) shrinkage temperature, (b) tensile strength, (c) tear strength, and (d) elongation at break

This study determined that tannins extracted from cashew fruit displayed a greater shrinking temperature in comparison to the control treatment (mimosa). Ukoha *et al.* (2010) stated that cashew fruit has condensed tannins that are similar to those in quebracho. The chemical structure of a substance and how well it can get into the collagen matrix and form stable bonds affect how well it can tan. The higher shrinkage temperature seen in cashew fruit tannins probably means that they can link very well. Ukoha *et al.* (2010) showed that the tannin level in cashew fruit is higher than that in mimosa. The binding of more tannin to collagen during the tanning process makes cashew-tanned leather more stable at high temperatures. The funnel plot for shrinkage temperature (Figure 4a) shows symmetry, which means that publication bias probably won't change the results of the study

**Tensile Strength**

We tested the tensile strength to see how well tanned leather could stand up to tearing. Twenty-four trials (Figure 5) showed that there were no big differences between non-mimosa vegetable tannins and the mimosa control. The combined analysis produced a p-value of 0.506, signifying statistical insignificance (Table 3). Unango *et al.* (2021) performed a study using *H. abyssinica* tannins, revealing a markedly reduced tensile strength relative to the control (Figure 6a). This extract has condensed tannins, which are usually linked to better leather

performance. However, the lower tensile strength may be due to the fact that the treated hides had more fat, which could make it harder for the tannins to penetrate and establish bonds. The heterogeneity evaluation from Table 3 shows a Q statistic of 108.6, an I<sup>2</sup> of 86%, and a  $\tau^2$  of 6.47. Together, these numbers show that the studies are very different from each other. The statistics suggest that the premise of a uniform genuine effect across trials is untenable; hence, the use of a fixed-effect model would be methodologically unsound. The Q value being much higher than its degrees of freedom (k - 1) means that the homogeneity hypothesis is wrong. An I<sup>2</sup> value greater than 75% indicates substantial heterogeneity, implying that the predominant observed variance is due to genuine differences in effect sizes rather than sampling error.

The tensile strength of fourteen plant species was evaluated. In the subgroup analysis, the cashew fruit was the only material that had a statistically significant effect compared to the control (mimosa), with a p-value of less than 0.001 (Table 3). Even though it was important, the tensile strength from tanning cashew fruit was lower than that from mimosa. There were no big changes between *Acacia nilotica*, *Plectranthus barbatus*, quebracho, and *Ceriops tagal* and the control group. These groups did not undergo statistical testing due to insufficient sample sizes (Table 3).

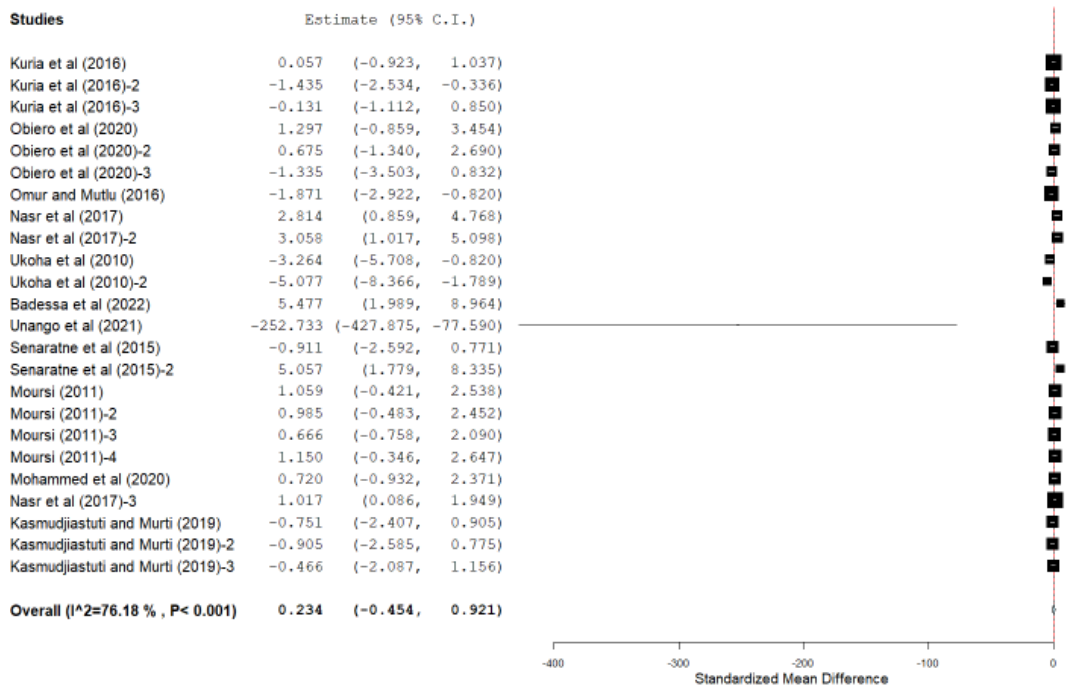


Figure 5. Forest plot of cumulative effect size (d++) with 95% confidence interval (CI) of the influence of vegetable tanning material on tensile strength

Table 3. Cumulative effect size (d++) with 95% confidence intervals (CI) for the influence of vegetable tanning materials on tensile strength across subgroups: (a) plant species, (b) animal species, and (c) hide/skin type.

Subgroup	Category	Estimate	Lower Bound	Upper Bound	Std. Error	p-Val
Plant type	<i>Acacia nilotica</i>	1.117	-0.360	2.595	0.754	0.138
	<i>Ceriops tagal</i>	-0.702	-1.656	0.252	0.487	0.149
	<i>Acacia xanthophloea</i>	-1.435	-2.534	-0.336	0.561	NA
	<i>Rumex abyssinicus</i>	0.720	-0.932	2.371	0.843	NA
	<i>Hagenia abyssinica</i>	-0.131	-1.112	0.850	0.501	NA
	Mango	0.666	-0.758	2.090	0.726	NA
	<i>Plectranthus barbatus</i>	0.229	-1.296	1.754	0.778	0.769
	Pomegranate	0.985	-0.483	2.452	0.749	NA
	Quebracho	0.727	-1.196	2.649	0.981	0.459
	<i>Emblica officinalis</i>	5.057	1.779	8.335	1.673	NA
	Cashew fruits	-3.909	-5.871	-1.948	1.001	<0.001*
	<i>H. abyssinica</i>	-252.733	-427.875	-77.590	89.360	NA
	Sodom apple	5.477	1.989	8.964	1.779	NA
	<i>Lawsonia inermis</i>	-0.911	-2.592	0.771	0.858	NA
Animal type	Sheep	0.763	-0.052	1.578	0.416	0.066
	Goat	-0.230	-2.178	1.717	0.993	0.817
	Fish	-0.702	-1.656	0.252	0.487	0.149
	Bufallo	1.900	-3.938	7.739	2.979	0.523
	Calf	-1.871	-2.922	-0.820	0.536	NA
Hide / Skin	Skin	0.281	-0.405	0.967	0.350	0.421
	Hide	0.308	-2.600	3.217	1.484	0.835
Overall		0.234	-0.454	0.921	0.351	0.506

Note: \*:Significant; NA: not analyzed

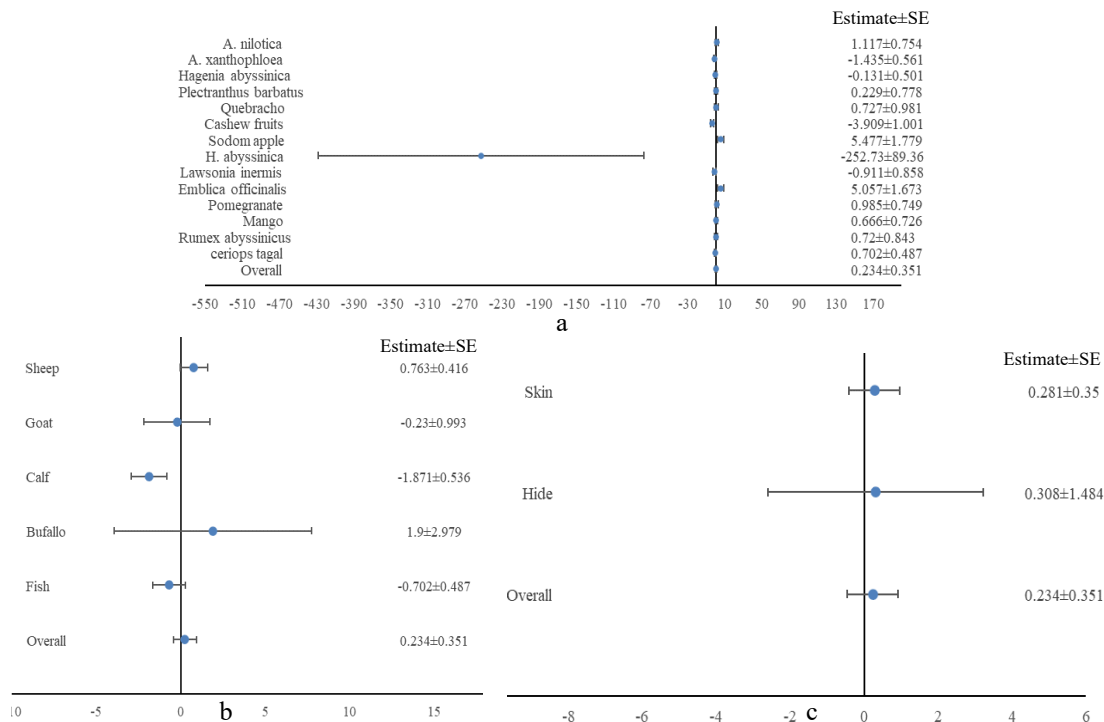


Figure 6. Forest plot of the cumulative effect size (d++) with 95% confidence intervals (CI) for the influence of vegetable tanning materials on tensile strength across subgroups: (a) plant species, (b) animal species, and (c) hide/skin type

Ukoha *et al.* (2010) said that the tannins in the cashew fruit husks are condensed tannins. Tannins can generate covalent connections with collagen, which makes the leather stronger. Mimosa and cashew fruit tannins are both condensed tannins, however they have different qualities. John (1997) emphasized that the tensile strength of leather is directly affected by changes in the kind and concentration of tannin. Moreover, research conducted by Liu *et al.* (2013) and Cheng *et al.* (2014) illustrates that the structural configuration of the skin's fiber network significantly influences the physical and mechanical properties of leather. The findings align with those of Suparno *et al.* (2012), who noted that fiber thickness, fiber orientation, and collagen fiber angles influence leather strength. Nalyanya *et al.* (2018) observed that the arrangement of collagen fibers is crucial for the development of tensile strength.

Subgroup analyses categorized by animal species and hide/skin types revealed no significant differences between non-mimosa tannins and the mimosa control (Table 3; Figures 6b and 6c). This result may be attributed to collagen being the primary structural component of the skin. Two kinds of reactive functional groups that cooperate with tanning treatments to make tanned leather more stable are carboxylates (COO<sup>-</sup>) and amines (-NH<sub>3</sub><sup>+</sup>) (Covington, 2019; Teklebrham *et al.*, 2012). The characteristics and magnitude of these interactions are crucial in assessing tensile strength. Figure 6b demonstrates that calfskin exhibited distinct features compared to other skin types. It wasn't done because there weren't enough research to assess for significance in this group. Figure 4b shows a symmetrical pattern in the funnel plot for tensile strength. This suggests that the dataset was not biased.

### Tear Strength

Tear strength describe how much tearing force leather can take before it breaks. A review of 21 trials indicated no significant differences between non-mimosa tannins and the mimosa control. The p-value was 0.649, which is more over the 0.05 level of significance (Figure 7 and Table 4). Figure 8a demonstrates that when we looked at the different types of plants, sodom apple had a considerably stronger tears than the other plant-based tannins and the control. But there weren't enough studies on this plant to run any further statistical tests. The Q value was substantially higher than the degrees of freedom (Q = 89.46; df = 17), which suggests that the studies were very different from each other. The I<sup>2</sup> value of roughly 81% shows that most of the changes we noticed are actual, not random sampling error. These differences could be attributable to the type of tanning material, the treatment methods, or the testing methodologies.

The tear strength of the plant-based tanning chemicals examined in this study is affected by several aspects, such as the kind and concentration of tannins. Tannins from sodom apple are known as condensed tannins, and they usually work better than hydrolyzable tannins (Badessa *et al.*, 2023). The type of tannin was similar to that of the control (mimosa), but the results were very different. Higher levels of tannin were linked to stronger tears, which is in line with studies on tanning with mimosa. Suparno *et al.* (2012) indicated that the mechanical qualities of leather, encompassing tear and tensile strength, are affected by variables such as hide thickness, fiber orientation, and the angle of collagen fibers in reference to the grain layer. Dellman *et al.* (1992) stressed that non-collagenous proteins in the skin can weaken tear strength by making it harder for tanning chemicals to bind to collagen.

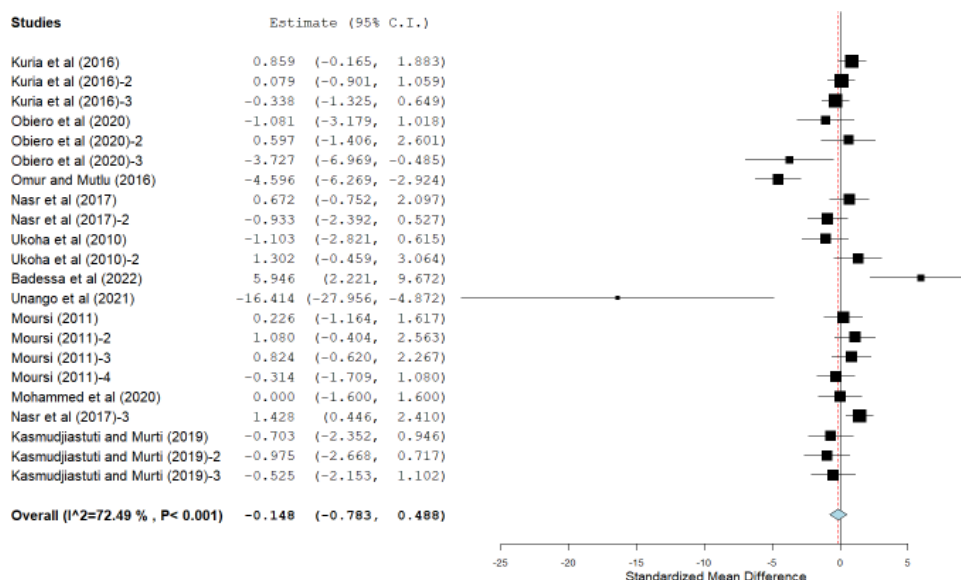


Figure 7. Forest plot of cumulative effect size (d++) with 95% confidence interval (CI) of the influence of vegetable tanning material on tear strength

Table 4. Cumulative effect size (d++) with 95% confidence intervals (CI) for the influence of vegetable tanning agents on tear strength across subgroups: (a) plant species, (b) animal species, and (c) hide/skin type

Subgroup	Category	Estimate	Lower Bound	Upper Bound	Std. Error	p-Val
	<i>Cerriops tagal</i>	-0.728	-1.684	0.228	0.488	0.135
	<i>Acacia xanthophloea</i>	0.079	-0.901	1.059	0.500	NA
	<i>Rumex abyssinicus</i>	0.000	-1.600	1.600	0.816	NA
	<i>Hagenia abyssinica</i>	-0.338	-1.325	0.649	0.504	NA
	Mango	0.824	-0.620	2.267	0.736	NA
	<i>Plectranthus barbatus</i>	-1.107	-3.297	1.083	1.117	0.322
	Pomegranate	1.080	-0.404	2.563	0.757	NA
	Quebracho	-1.044	-3.437	1.348	1.221	0.392
	<i>H. abyssinica</i>	-16.414	-27.956	-4.872	5.889	NA
	Cashew fruits	0.091	-2.266	2.449	1.203	0.939
	<i>Acacia nilotica</i>	0.645	-0.068	1.359	0.364	0.076
	Sodom apple	5.946	2.221	9.672	1.901	NA
	Sheep	0.333	-0.245	0.911	0.295	0.259
Animal	Fish	-0.728	-1.684	0.228	0.488	0.135
type	Calf	-4.596	-6.269	-2.924	0.853	NA
	Goat	0.105	-1.358	1.569	0.747	0.888
Hide /	Skin	0.099	-0.417	0.615	0.263	0.708
Skin	Hide	-4.596	-6.269	-2.924	0.853	NA
	Overall	-0.148	-0.783	0.488	0.324	0.649

Note: NA: not analyzed

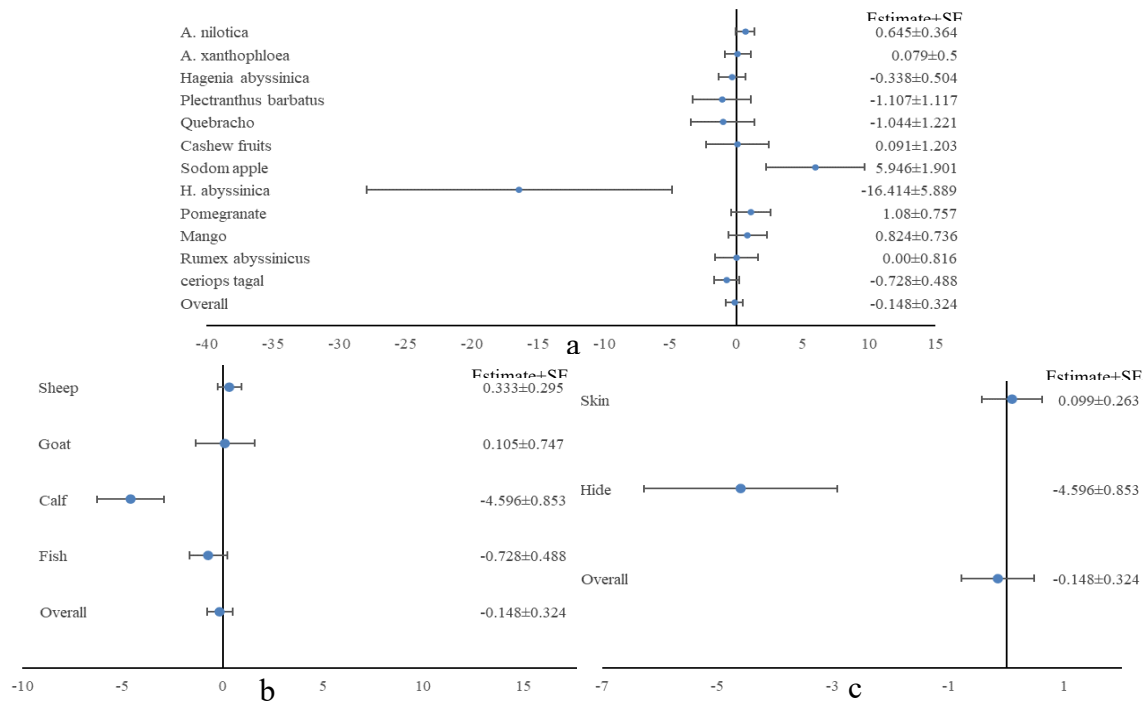


Figure 8. Forest plot of the cumulative effect size (d++) with 95% confidence intervals (CI) for the influence of vegetable tanning agents on tear strength across subgroups: (a) plant species, (b) animal species, and (c) hide/skin type

The subgroup analysis, which looked at different types of animals and hides/skins, showed that the tensile strength results were consistent across the groups. You can see this in Table 4 and Figures 8b and 8c. No significant differences were detected among any animal or skin category. Due to the lack of published studies, calf hides were not included in the statistical analysis. The funnel plot analysis

showed a symmetrical distribution, which means that there was no publication bias in the dataset (Figure 4c).

#### Elongation at Break

Elongation at break measures how much leather changes shape when it is under tensile stress before it breaks. It is also a basic way to assess how

elastic a material is. The results showed that there was no significant difference in elongation at break between the treatments, with a p-value of 0.680, which is higher than the 0.05 significance level (Figure 9 and Table 5). This means that leather tanned with different vegetable tannins has about the same amount of stretch. Table 5 shows that a Q-value of 41.45 with 15 degrees of freedom led to an  $I^2$  of 63.9% and a  $\tau^2$  of 0.54. This means that the studies were moderately to quite different from each other. The observed heterogeneity suggests that differences in effect magnitude are not just due to random fluctuations. The variances could be due to things like the type of tanning substance used, the conditions of the experiment, or changes in the study design.

Li *et al.* (2018) demonstrated that the elastin content in animal skin influences its stretchability, with increased elastin levels generally improving the elongation at break of the resulting leather. This research assessed the impact of ten tannin-producing plant species on elongation at break. The subgroup analysis revealed that only two species, quebracho and *Acacia nilotica*, demonstrated significant changes in comparison to the control (mimosa) (Table 5 and Figure 10a). The other sources of tannin were not significantly different from the control. However, the modest sample sizes made it unable to do more statistical analysis.

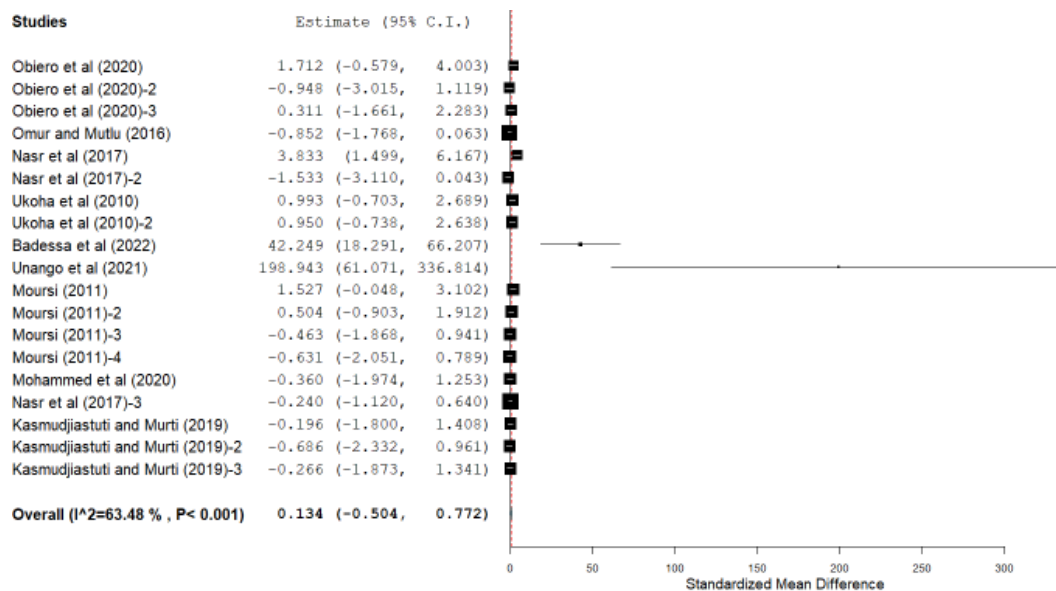


Figure 9. Forest plot of the cumulative effect size (d++) with 95% confidence intervals (CI) for the influence of vegetable tanning agents on elongation at break

Table 5. Cumulative effect size (d++) with 95% confidence intervals (CI) for the influence of vegetable tanning agents on elongation at break across subgroups: (a) plant species, (b) animal species, and (c) hide/skin type

Subgroup	Category	Estimate	Lower Bound	Upper Bound	Std. Error	p-Val
Plant type	<i>Ceriops tagal</i>	-0.378	-1.312	0.557	0.477	0.428
	<i>Quebracho</i>	-0.667	-1.211	-0.123	0.277	0.016*
	<i>Rumex abyssinicus</i>	-0.36	-1.974	1.253	0.823	NA
	<i>Acacia Nilotica</i>	2.513	0.277	4.748	1.141	0.028*
	Mango	-0.463	-1.868	0.941	0.717	NA
	Cashew fruits	0.971	-0.225	2.168	0.610	0.112
	Pomegranate	0.504	-0.903	1.912	0.718	NA
	Sodom apple	42.249	18.291	66.207	12.224	NA
	<i>Plectranthus barbatus</i>	0.294	-1.157	1.745	0.740	0.691
	<i>H. abyssinica</i>	198.943	61.071	336.814	70.344	NA
Animal type	Goat	0.555	-0.774	1.885	0.678	0.413
	Sheep	0.290	-0.845	1.425	0.579	0.617
	Calf	-0.852	-1.768	0.063	0.467	NA
	Fish	-0.378	-1.312	0.557	0.477	0.428
Hide / Skin	Skin	0.225	-0.458	0.908	0.349	0.519
	Hide	-0.852	-1.768	0.063	0.467	NA
Overall		0.134	-0.504	0.772	0.325	0.680

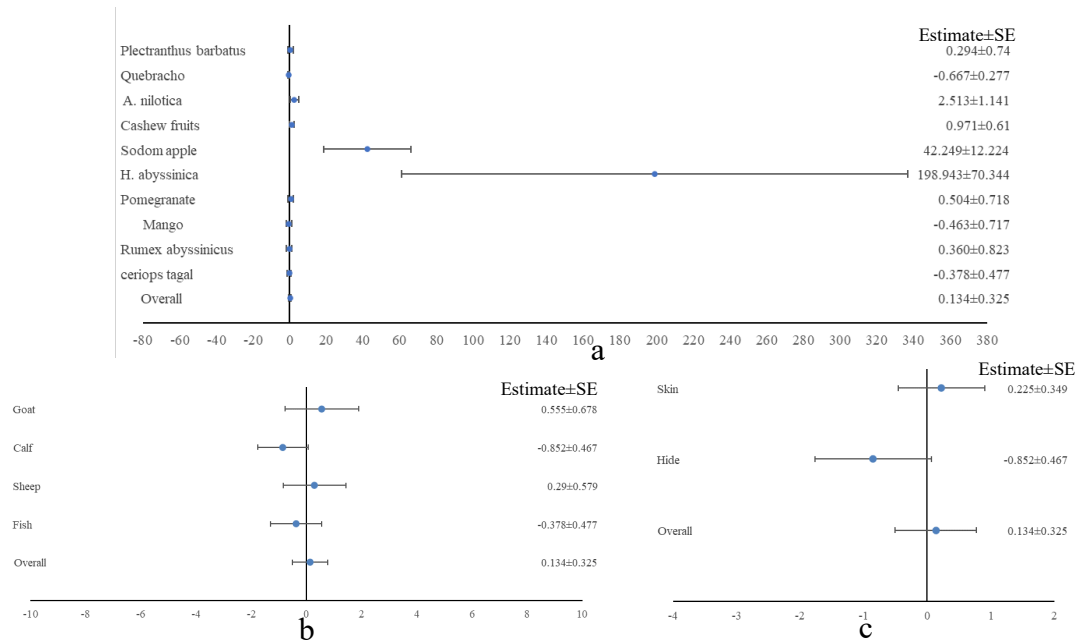


Figure 10. Forest plot of the cumulative effect size ( $d^{++}$ ) with 95% confidence intervals (CI) for the influence of vegetable tanning agents on elongation at break across subgroups: (a) plant species, (b) animal species, and (c) hide/skin type

The elongation value of quebracho-tanned leather was lower than that of the mimosa control, while *Acacia nilotica* exhibited a greater elongation value (-0.677 and 2.513, respectively; Table 5). The reduced elongation observed in quebracho is probably a result of the strong crosslinking between its tannins and collagen fibers, leading to structures that are less flexible and more rigid (Moursi 2011). Tanning with *Acacia nilotica* made the material longer, probably because its hydrolyzable tannins make collagen more flexible. Previous studies by Nasr *et al.* (2017), Mahdi *et al.* (2006), El Sissi *et al.* (1967), Malan *et al.* (1991), Dube *et al.* (2001), and Sundaram *et al.* (2007) have shown that *Acacia* tannins may come in condensed, hydrolyzable, or mixed forms.

Hydroxyl groups in tannins can give and take functional groups from collagen, such as carbonyl, amide, and hydroxyl groups, which are found in serine and tryptophan. The creation of hydrogen bonds forces water molecules out of the collagen matrix, making the fibers thicker and stiffer. Tannins can make covalent connections with collagen. After being oxidized to quinones, these reactive intermediates can attach to the amino groups (-NH<sub>2</sub>) of lysine, the thiol groups (-SH) of cysteine, and the imidazole ring of histidine (Covington & Wise, 2019). Leather made by covalent crosslinking has better temperature resistance since these linkages are stable.

*Acacia nilotica* tanning resulted in superior elongation values relative to the control treatment. The observed effect is likely due to hydrolyzable tannins in *A. nilotica*, which are known to make

interactions with collagen fibers more flexible instead of stiff crosslinks. Studies by Nasr *et al.* (2017), Mahdi *et al.* (2006), El Sissi *et al.* (1967), Malan *et al.* (1991), Dube *et al.* (2001), and Sundaram *et al.* (2007) demonstrate that tannins from *Acacia* species can be categorized into condensed, hydrolyzable, or mixed types.

Subgroup analyses based on animal species and skin type confirmed these results, showing that there were no major differences in elongation at break between different animal hides or skin types (Figure 10b and 10c; Table 5). The findings indicate that the elongation characteristics of vegetable-tanned leather are predominantly affected by the interactions between tannins and the reactive groups in collagen, as well as the inherent elastin content in the skin. The funnel plot evaluation demonstrated that the dataset employed in this analysis was free from publication bias (Figure 4d).

### The Potential of Vegetable Tannins in Indonesia

Indonesia has a lot of potential for developing vegetable tannins because it has a lot of biomass resources that are high in tannin compounds. The bark from industrial plantation species like *Acacia mangium* and *A. auriculiformis*, gambir plants that grow a lot in Sumatra, and several mangrove species, especially *Rhizophora* and *Cerriops*, are all primary sources. These plants are often not used or are thought of as waste (Mutiar and Kasim, 2023; Pancapalaga *et al.*, 2023; Pazla *et al.*, 2025). These raw materials could be good substitutes for imported tanning chemicals and could help the domestic vegetable tanning industry grow, especially if there are

localized extraction facilities and standardized extract quality.

From an industrial point of view, the global shift to chrome-free and environmentally friendly leather creates a lot of market prospects for vegetable-tanned products. Research in Indonesia demonstrates that extracts from *acacia* and gambir can produce leather that meets national quality standards for specific purposes. The use of clean tanning processes using vegetable tannins from the area may make exports more competitive, reduce environmental damage, and raise the economic worth of the forestry and plantation industries.

## CONCLUSIONS AND RECOMMENDATIONS

### Conclusions

The results of this study show that non-mimosa vegetable tanning agents don't change the physical or mechanical properties of tanned leather in any significant way. This includes shrinkage temperature, tensile strength, tear strength, and elongation at break, compared to traditional mimosa-based treatments. The type of tannin in the plant source has the biggest effect on the quality of tanned leather. Moreover, variations in animal species or skin type (hide/skin) did not substantially influence these findings.

These results indicate potential directions for future research. Further investigation into the effects of different tannin classes, particularly condensed and hydrolyzable tannins, would improve understanding of how tannin chemistry affects the quality of leather. Investigating mixed tannin systems, such as *Acacia nilotica*, may provide valuable insights, as these combinations could attain an optimal balance of flexibility and strength for various leather applications. Additionally, examining the interactions between tanning agents and the microstructural attributes of collagen, including fiber orientation, thickness, and elasticity, may facilitate the development of techniques to enhance critical mechanical properties and produce more durable leather.

### Recommendations

This study suggests the enhancement of meta-analysis research concerning tannin kinds and alternative tanning chemicals to gain a deeper comprehension of their impact on the physical and mechanical qualities of leather.

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