EVALUATION OF THE TANNING VIABILITY OF TANNINS FROM COFFEE PULP IN THIKA SUB-COUNTY, KIAMBU COUNTY, KENYA.

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DEPARTMENT OF PUBLIC HEALTH, PHARMACOLOGY AND TOXICOLOGY

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DECLARATION

This Thesis is my original work and has not been presented for a degree in any other University

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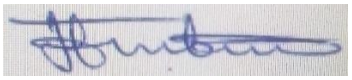
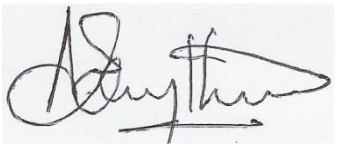
Prof. Jackson N. Ombui (BVM, MSc PhD) Department of Public Health, Pharmacology and Toxicology, University of Nairobi		10.04.2022
Dr. Arthur Onyuka PhD Kenya Industrial Research and Development Institute (KIRDI		08/04/2022

DEDICATION

This work is dedicated to Agnes my mother for her prayers and support and to God who helped me conduct this work.

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LIST OF ABBREVIATIONS

BIS - Bureau of Indian Standards.

DPHPT- Department of Public Health, Pharmacology and Toxicology.

IUP - Physical Test Methods.

IULTCS- International Union of Leather Technologists and Chemists.

KIRDI- Kenya Industrial Research and Development Institute.

N/mm^2- Newtons per square millimeter.

UNIDO- United Nations Industrial Development Organizations**.**

ABSRACT

The tanning industry utilizes chrome salts for tanning despite them being considered environmental pollutants. Vegetable tanning is considered to be a greener alternative to chrome tanning with mimosa extract being the most commonly used. The presence of inadequate acacia trees in Kenya for mimosa production means that the country majorly relies on imports which results in an increase in their prices leading to an increase in cost of production. This study was formulated to determine the viability of coffee pulp as a source for vegetable tannins. Twelve samples were collected from Yadini coffee factory in four different days. The tannin content was quantitatively determined by the hide powder method. The quality of the leathers was determined by carrying physical tests on tanned goatskins according to IUP methods. A statistical t test was used for comparison of *coffea arabica* pulp and mimosa tannin content and physical properties of resultant leathers. It was established that *C. arabica* pulp had a tannin content of 5.04% and a tanning strength of 2.26 compared to mimosa extract with a tanning content of 64% and a tanning strength of 2.82 with the two tannins being of the condensed type. This showed that there was a significant difference ($p<0.05$) between the tannin content and tanning strength of mimosa and *C. arabica* tannins. The physical characteristics of *C. arabica* pulp tanned leather was $\uparrow$14.72±2.22N/mm^2 and $\rightarrow$19.09±1.60N/mm^2 tensile strength, 62^{o}C shrinkage temperature, $\uparrow$48.00±14.15 N/mm, $\rightarrow$38.12±3.13N/mm tear strength, grain crack and grain burst of 4.52±0.31mm and 5.93±0.28mm respectively and a change in colour at 100000 flexes for flex endurance. Mimosa tanned leather had $\uparrow$24.19±2.25N/mm2 and $\rightarrow$27.20±3.26N/mm^2 tensile strength, 83^{o}C shrinkage temperature, $\uparrow$75.97±8.68N/mm, $\rightarrow\rightarrow$72.08±8.19N/mm tear strength, grain crack and grain burst of 7.47±0.09mm and 8.25±0.15mm respectively. There was no damage at 100000 flexes for flex endurance. The t test used for comparison showed that there was a significant difference ($p<0.001$) for tensile strength, tear strength, shrinkage temperature, ball

burst and flex endurance. The study concluded that the tanning strength of coffee pulp was more than the minimum 1.5 recommended for vegetable tanning materials. The physical properties exceeded the minimum recommended limits although they were less comparable to mimosa tanned leather. It was recommended that further research to be conducted on the penetration of *C. arabica* pulp tannins in the pelt as the coffee tannins in their natural form did not penetrate making their use in tanning in this state difficult.

CHAPTER 1. INTRODUCTION

1.1. Background

Tanning is the transformation of an organic material liable to decay into a stable material that resists putrefaction by bacteria with an increase in the hydrothermal stability and unique physical and chemical modifications imparted on tanned hides and skins by the tanning agent (Yao *et al*., 2019). The organic material referred here is the hides and skins that are gotten as one of the waste items of the meat industry. These hides and skins are mainly gotten from cattle, sheep and goats in Kenya, although ostrich skins, fish skins and skins from crocodiles are available. There are two main types of tanning; mineral tanning and vegetable tanning (Maina *et al*., 2019), the most common of the mineral tanning is chrome tanning which can be traced back to just over 100 years ago. It has been the most widely used tanning agent in the recent past because chromium forms leather with a hydrothermal stability of more than100 ^{o}C which is very versatile(Liu *et al*., 2019). This benefit is however compared to the effects that the resultant wastes produce. These wastes range from solid tanned wastes, liquid wastes to sludge (Hu *et al.,* 2011; Rigueto *et al.,* 2020). Control measures have been put in place i.e., to see whether the uptake of chrome can be maximized so as to reduce the percentage of chrome in wastes. However, this has proven to be a difficult task as complete uptake of chromium has been difficult to achieve (Pradeep *et al.,* 2021). The uptake increment also only solves the problem in liquid wastes and sludge but fails to solve it in solid wastes.

Mimosa has been the most commonly and widely used vegetable tannin in the world especially in production of heavy leathers such as sole leathers. However, in Kenya, mimosa that is used is mainly from imports as there aren't enough acacia trees to support local production of these tannins resulting in an increase in their price and eventually an increase in the cost of production. Some studies were carried out in Kenya in search of alternative

sources for vegetable tannins. Kuria, (2015) studied various vegetable tannins in Laikipia county Kenya to ascertain their tanning potential. The study found that *Acacia xanthophleo*, *Acacia nilotica* and *Hagenia abyssynica* had enough tannins for commercial extraction. Kimaiga, (2016.) studied *Plectranthus barbatus* as an alternative source. Although these studies showed that these plants had sufficient vegetable tannins for extraction, the availability of these plants in sufficient quantity to sustain production is still not enough. It is for this reason that this study was carried out to search for an alternative vegetable tanning material that is available in sufficient quantities for production.

1.2.Problem statement

Chrome tanning is known to cause environmental pollution globally because the chromium offered into the tanning drum is not completely utilized and end up in the effluent (Ozgunay *et al.,* 2018). High concentration of this compound in the effluent complicates the treatment process and hence more cost is incurred. Chrome waste occurs in three forms, i.e. liquid waste, solid tanned waste and in sludge(Sundar *et al.,* 2011). According to Liu *et al*., (2019), approximately 70% of chrome salt added to the tanning liquors is absorbed by the pelt and the remaining more than 30% is released into the effluent. When chrome is discharged in even low amounts, it is very toxic as it interferes with daphnia thus disrupting the fish food chain and even the photosynthesis of aquatic plants (Wu *et al.,* 2012). It also adversely affects human health if ingested or inhaled. The pickling process that precedes tanning proper for chrome tanning uses sodium chloride which is drained into the effluent. Salt is known to have very high detrimental effects to every environmental sphere that it is disposed to due to its salinity levels which tend to destroy all kinds of vegetation around it and in fresh aquatic environment. According to Zhang *et al.,* (2017), the high salt levels tend to dehydrate the aquatic animals such as fish to death. As stated before, the conventional tanning methods have more negative effects on the environment as compared to the vegetable tannings. When

it comes to vegetable tannins, different tannins have a varied degree of ecotoxicity to the aquatic environment and human toxicity, e.g., mimosa is more toxic to the aquatic environment as compared to gambier tannins. However, gambier is more expensive compared to mimosa (Alfarisi and Ciptomulyono, 2016). Thus, there is need for a vegetable tannin which has low aquatic ecotoxicity and easily available.

1.3.Objectives

1.3.1. General objective

To evaluate the tanning viability of coffee pulp from *Coffea arabica* in Yadini farm, Kiambu County, Kenya.

1.3.2. Specific objectives

i. To identify the type of tannins, present in pulp of *Coffea arabica* grown in Yadini farm, Kiambu County, Kenya.
ii. To determine the tannin content and tanning strength of *Coffea arabica* pulp.
iii. To compare the physical characteristics of goatskin leather tanned with *Coffea arabica* pulp and goatskin leather tanned with standard commercial mimosa.

1.4. Research Hypothesis

Ho: *Coffea arabica* pulp contains sufficient tannin content and strength for effective tanning of leather.

$H_{1:}$ *Coffea arabica* does not contain sufficient tannin content and strength for effective tanning of leather.

1.5. Justification

Scientists have been able to see the effects of chromium tannage wastes to the physical environment and the biological environment. Vegetable tannage has been proposed as a suitable replacement for chrome tannage and may as well be applicable to all other forms of mineral tannage. However, vegetable tannins, although available in Kenya, are slightly higher priced as compared to basic chromium salts. This coupled with the fact that chromium tanning uses 6-8% of chrome salts whereas the vegetable tanning uses 10-15% of tannins which is approximately twice the amount used in chromium tanning leads to an increase in cost of production which limits the profit margin for companies hence most small-scale industries opt to use chrome salts. Tannins from coffee pulp would be a viable option due to their availability as the coffee industry produces a lot of pulp as a byproduct. Coffee pulp has been found to possess bioactive materials such as tannins which can be used in leather manufacture. The byproduct is readily available in large quantities which will translate to high amounts of coffee pulp tannin. The free source of coffee pulp will ensure that the market prices for coffee pulp tannin is cheaper making tanning a cheaper enterprise as compared to other vegetable tannins. It is for this reason that the study was undertaken to seek out a different tannin material with the same or better qualities as compared to the conventional tannins but which will be both cheap and readily available for most small-scale tanners.

CHAPTER 2. LITERATURE REVIEW

2.1. A Historical Overview of Tanning

The conversion of hides and skins into leather is an old craft that has been practiced since Neolithic time to ensure that these materials do not decay (Falcão and Araújo, 2011). In these ancient times, the tanning material which was employed was vegetable tannins otherwise referred to as plant polyphenols, before the introduction of chrome salts around 150 years ago (Sundar and Muralidharan, 2017). This is the main reason why leathers in museums and collections are mainly vegetable tanned (Sebestyén *et al.,* 2019). People who lived in those ancient times learned the craft from experience. The word tannin was first used by Seguin in 1796 to describe the ability of a plant extract to convert a hide or skin into leather and it originated from the word oak from the Celtic language(Sivakumar *et al.,* 2007). The oak was the first known species which was employed in the tanning of hides and skins into leather. Swain and Bate-Smith were the ones who gave vegetable tannins a proper definition when in 1962 they described them as polyphenolic compounds which occur naturally and possess molecular weights between 500 and 3000 and are able to precipitate alkaloids, gelatin and other proteins from aqueous solutions (de Hoyos-Martínez *et al.,* 2019) Since the introduction of chrome salts for tanning, the tanning industry has adopted chrome salts as their primary tanning material with over 80% of leather currently being processed with chrome salts and the remaining mostly utilized the vegetable tanning material (Pradeep *et al.*, 2021).

There are various tanning methods which are employed in the tanning of hides and skins into leather. These include mineral tanning with chrome salts being the most used mineral tannage, the use of syntans, vegetable tanning and combination tanning.

2.2.Chromium Tanning

Mineral tanning is one of the most important processes in the conversion of hides and skins into leather with chromium salts being the most important mineral tanning agents although titanium and aluminum have been found to contain some tanning characteristics (Andreyeva *et al.,* 2017). Chrome tanning although discovered around 150 years ago is widely used in leather manufacture as compared to vegetable tanning with nearly 90% of leathers worldwide being processed with chromium salts and the remaining mostly being tanned with vegetable tannins (Zhu *et al*., 2020). The two chromium species that are relevant in leather industry with tanning properties are trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) chromium with trivalent chromium being oxidized into hexavalent chromium under certain environmental conditions though in rare cases (Zhu *et al*., 2020). Trivalent chromium is used in tanning as it has tanning properties whereas hexavalent chromium is highly avoided as it was discovered to be carcinogenic(Basaran *et al.,* 2008). After tannage with chromium, the pelt that is white in colour (the colour of collagen) is transformed into a blue material which is commonly referred to as wet blue leather and is characteristic of chrome tanning. The use of chromium salts for tanning, although produces leathers with superior qualities and are versatile, faces problems on the environmental front due to the effect of chromium on the environment and human health.

2.3.Vegetable Tanning

Vegetable tannins are described as extracts of plant materials. They are polyphenolic compounds with molar mass between 500 and 20000 Daltons and are soluble in water (China *et al.,* 2020b; Grasel and Ferrão, 2016) . These tannins are found in leaves, stems, barks, fruits and pods of various plants and are regarded as secondary metabolites as they are mainly produced by plants to defend them from external harm (Arbenz and Avérous, 2015). The content of these tannins is said to differ in a plant according to the part of the plant taken such

as leaves, fruit or stem with variations also being observed for the same type of plant from different environments. Factors such as availability of water also affect tannin contents in plants with more quantities being found in areas where the presence of water is minimal and in different seasons (de Hoyos-Martínez *et al.*, 2019). According to Auad *et al.,* (2020) vegetable tannins have gathered a lot of interest in industrial processes but the main economically viable option is their use in leather manufacture since they have the ability to bind with protein in hides and skins to produce leather (Zywicki *et al.*, 2002) . Tannins are fixed on the hide protein by hydrogen bonds when the pH is between 2-8. Upon binding themselves to collagen in hides and skins they increase the flexibility of the leather and protect it from microbial action (Kemppainen *et al.,* 2014). The efficiency of a tannin material is dependent on the molecular weight of the tannin which must be between 500 to 3000 Daltons because those tannins that tend to have higher molecular weights tend to be unable to penetrate into the fiber structure of the skin and are insoluble while those with lower molecular weights lack astringency (Combalia *et al.*, 2016a). Tannin are able to tan due to the presence of various reactive groups and a sufficient size so as to bind several fibers together (Combalia *et al.*, 2016b). The interactions between tannins and collagen, have been reported to affect the solubility, secondary and tertiary structure of the protein and thermal stability which affects the physical and mechanical properties of leather. It is also important to note that the affinity of tannins for proteins is said to depend on the types of proteins as well as their hydrophobicity, isoelectric point, amino acid composition and also the structure of the phenolic compounds (Cano *et al.,* 2020). The tannins, in the tannage step, diffuse into the animal skin and interact with the collagen of the skin. This leads to stabilization of the animal skin with tannin extracts containing higher tannin content having a higher efficacy in tanning(Maier *et al.,* 2017a). The molecular weight of the tannin is very important as the penetration of large sized molecules is reduced which in effect lowers the thermal stability or

the tanning effect. Molecules which are also too small cannot crosslink with collagen peptide chain, resulting to no tannin effect (Qiang *et al.,* 2018). Tanning using vegetable extracts requires that the extracts be in contact with the skins for a considerable amount of time. This is because vegetable extracts are composed of organic molecules with different molecular sizes that tend to be joined together, thus, increasing the size of the tanning agent which makes the penetration and fixation of the vegetable tanning material more difficult (Combalia *et al.*, 2016b).

2.4.Classification of Vegetable Tannins

Vegetable tannins has been classified into three categories: hydrolysable tannins, condensed tannins and complex tannins. Hydrolysable tannins can further be subdivided into ellagitannins and gallo-tannins (Arbenz and Avérous, 2015). The production of vegetable tannins highly favours the condensed tannins as data shows that of the annual production of 200000 tons, over 90% are condensed tannins with the remaining being hydrolysable tannins(Kemppainen *et al.*, 2014).

2.4.1. Hydrolysable Tannins

The first category of hydrolysable tannins is mainly characterized by esters of phenol carboxylic acid which stop the condensed tannins from undergoing oxidation and are used to make light coloured vegetable tanned leathers(Sivakumar *et al.,* 2007). 1,2,3-trihydroxybenzene referred to as pyrogallol gives this class of tannins the name pyrogallols and forms the basis for the building of the structure for hydrolysable tannins (Sebestyén *et al.,* 2019). Hydrolysable Tannins are subdivided into gallotannins and ellagitannins.

Gallotannins are hydrolysable polyphenols in which the glucose core is esterified only with gallic acid although the gallate groups can esterify themselves at the phenolic hydroxyls (Silva *et al.,* 2020).

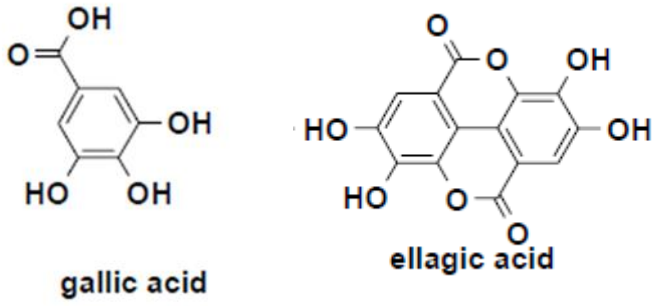

Figure 2.1: Gallic acid and Ellagic acid (Hagerman 2002.)

Ellagitannins are hydrolysable polyphenols where the esterified moieties include gallic acid, ellagic acid and chebulic acid. Leathers which are produced by hydrolysable tannins tend to be pale yellow, greenish or brown and are light fast. These hydrolysable tannins are mostly found as gallotannins which are multiple esters with D-glucose and are associated mainly with woody and herbaceous dicotyledonous plants(Haslam, 2007). They tend to undergo hydrolysis in the presence of acids or enzymes and are hydrolyzed by weak acids or bases to produce a carbohydrate and phenolic acids(Shirmohammadli *et al.*, 2018).

2.4.2. Condensed Tannins

The chemical structural basis for condensed tannins is flavan-3-ol. They are flavonoids which have undergone polymerization or oligomerization and are also referred to as proanthocyanidins which are considered to be polymeric flavonoids(Falcão and Araújo, 2014). The flavonoids are basically a wide ranged group of metabolites that are based on a heterocyclic ring system (Haggerman, 2002).

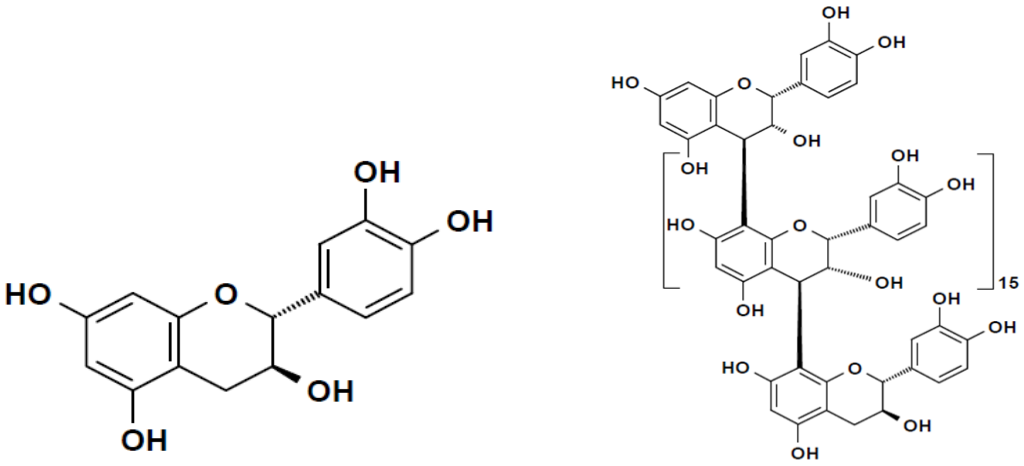

Figure 2.2: Flavan-3-ol structure and epicatechin-[(4β->8)-epicatechin]$_{15}$ –(4β->8)-catechin (Hagerman, 2002)

When the condensed tannins exist as oligomers, they can be made up of two monomers or even up to ten monomers as shown in the structure of epicatechin –[(4β->8)-Epicatechin]$_{15}$ -(4β->8)-catechin below. The solubility of condensed tannins depends on whether they are polymeric or oligomeric in form with the polymeric form having little to no solubility at all whereas the oligomeric form are soluble in water (Martins *et al.,* 2020). Condensed tannins do not undergo hydrolysis but rather undergo oxidation and polymerization forming phlobaphenes also referred to as reds and are insoluble in water (Kuria, 2015).

2.5.Extraction of Vegetable Tannins

Vegetable tannins are extracted from various parts of plants where they have been identified. The extraction process is very important as it determines the purity of the tannins obtained and the quantity of the yield. There hasn't been a universal way of extraction of tannins due to their heterogenous nature and because rarely does the extraction yield the tannins only. They are normally obtained with other compounds such as non-tans(de Hoyos-Martínez *et al.*, 2019). The non-tans present in tanning liquors include acids and their salts, hemicellulose and sugars with the acids and their salts being very important as they control the astringency of the liquor and the entire tanning process (Reeds, 1969).

The extraction of tannins for the leather industry is mainly done with water alone as the solvent or together with other organic solvents such as methanol, ethanol, acetone and sodium hydroxide. Methods which have been studied include extraction with hot water, the use of ultrasound and microwave to assist in the extraction of these tannins, use of ionic fluids, maceration, use of supercritical fluids, decoction, (Das *et al.,* 2020; de Hoyos-Martínez *et al.,* 2019).

The use of solvents in the extraction of tannins can be summarized into one method which is referred to as solid liquid extraction. This method is conducted by allowing the vegetable material to interact with the solvent without any further assistance and as a result the solvent enters the cell wall of the vegetable material to dissolve the tannins and transports them out of the material. The extraction of tannins for the leather industry is conducted through open diffusion as it is done on an industrial scale. Water is normally used as the preferred solvent due to environmental concerns although methanol is also a suitable solvent as both water and methanol are polar solvents and the extraction of tannins is dependent on the polarity of the solvent that is used (de Hoyos-Martínez *et al.,* 2019).

The water extraction is conducted by increasing the temperature and the pressure to subcritical conditions and maintaining the solvent which is water as a liquid and in result reduces the polarity, viscosity, surface tension and dissociation constant of water as compared to water under normal conditions. This in effect ensures that more tannins are moved from the plant material being extracted and also takes less time as compared to solid liquid extraction(Xuan Cuong *et al.,* 2020). The use of pressurized hot water for tannin extraction could be well suited for the leather industry due to the high yields as water is said to yield more tannins than the use of organic solvents such as methanol together with the added advantage that water is cheaper as compared to these solvents(Mohd Jusoh *et al.,* 2019).

Maceration and decoction are used for medicinal plants with decoction being macerated by continuous heating at 100^{o}C with organic solvent or water.

The use of ultrasound is to enhance the solid liquid extraction by increasing the mass transfer of the tannins from the plant material and the liquid media through power cavitation which encourages the strongly bound tannins to detach themselves from the plant material. As a result, more tannins move to the liquid media. The plant materials are well utilized through thorough extraction of tannins thus ensuring that there isn't any waste of these tannins(Sivakumar *et al.*, 2014).

2.6.*Coffea* Plant

Coffea plant which traces back its heritage to Ethiopia as a beverage is currently the world's most favorite beverage with 2018 figures showing that over 9 million tons of coffee was put up for sale in the market (Kamil *et al.*, 2019). Due to its large consumption, the coffee crop is among the most important cash crops in the world with it being cultivated mostly in the tropical areas. *Coffea* plant belongs to the family *Rubiaceae* which has over 400 genera and over 4800 species. The Genus *Coffea* has two species which are commonly used for making coffee beverage and are commonly cultivated although there are over 80 species in the genus (Das and Venkatachalapathy, 2016).

Plate 2.1: *Coffea arabica* plant grown in Yadini coffee farm

These are *C. arabica* which is commonly known as Arabica coffee and *C. canephora* also known as Robusta coffee. In the global market, *C. arabica* is predominant with a share of 64.5% with the remaining being *C. robusta* (Gemechu, 2020; Mohammed *et al.*, 2016). The global production of coffee being over 9 million tons in 2018-2019 and increasing to 10.5 million tons in 2019-2020, means that there is also a subsequent increase in the production of by products from the coffee (Oktaviani *et al.,* 2020). This production of coffee waste translated into quantities means that for every 1 ton of coffee cherry processed 600kg are recovered as waste (Krishna Murthy *et al.*, 2019). The by products are obtained from the primary and the secondary processing stages in coffee processing with the primary stage aiming to get the green coffee bean and the secondary stages purposing to further process the green coffee bean into roasted coffee. There are two methods that are used for the primary processing which are the wet method in which the pulp is mechanically removed and the bean dried and the dry method where the cherries are dried with the pulp still present (Gemechu, 2020; Rajesh Banu *et al.*, 2020). The wet method produces the pulp while the dry method produces a husk as a byproduct. The main byproducts of coffee processing are the skin, pulp/husk and silverskin with the silverskin being the main byproduct of roasting and the rest being from the primary stage(Janissen and Huynh, 2018).

2.7. Coffee Cherry Anatomy

The coffee plant yields a fruit which can be described as a berry or cherry and it comprises of the outer skin or pericarp which is normally green when unripe and red when ripe. This covers the pulp which is yellowish in colour and referred to as outer mesocarp. The pulp lies next to the mucilage also called pectin layer and is colourless and highly hydrated. The mucilage is followed by the parchment or endocarp which is also yellowish in colour but thin. The endocarp lies next to the silverskin which covers the endosperm or coffee bean (Esquivel, 2012).

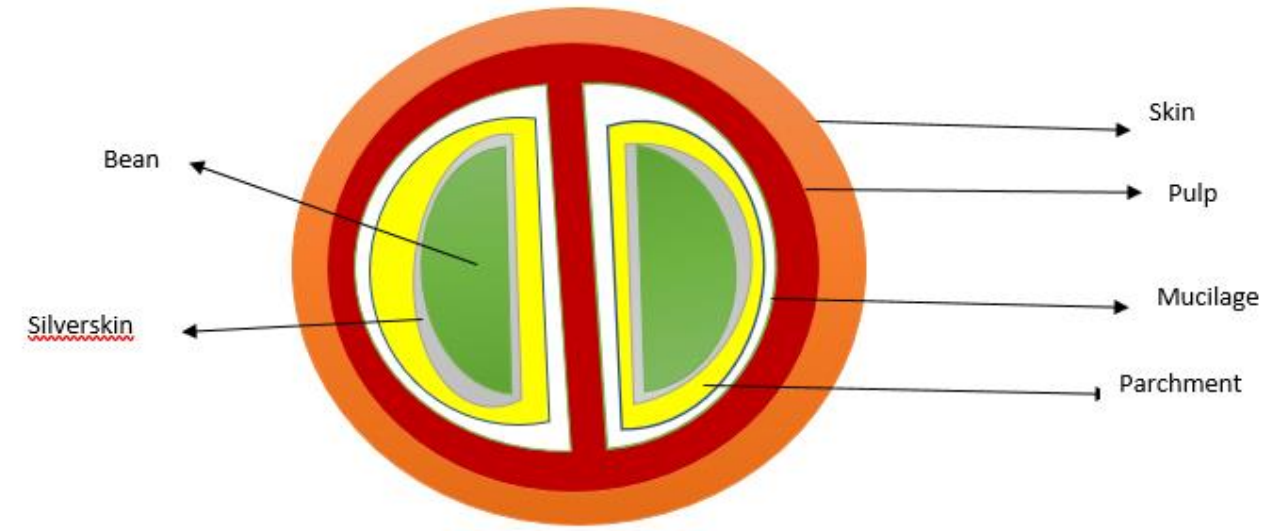

Figure 2.3: The Structure of Coffee berry (Santos *et al.*, 2021)

2.8.Post-harvest processing of coffee

After the harvesting of coffee cherries, they are processed in a series of processes in order to acquire the bean which is further processed to make coffee powder used to make the beverage. The processing of coffee is classified into three stages which are the primary, the secondary and tertiary processing stage with the primary stage being the one that produces green coffee beans and in the process producing coffee pulp or husk(Chanakya and De Alwis, 2004). Post-harvest processing can generally be classified into two processes, the wet and dry processes as previously stated. The dry process keeps the fruit intact while the wet process can be done in three ways. This is either by just removing the bark and part of the mucilage (referred to as peeled cherry), removing by mechanical means the bark and the mucilage or by mechanically removing the bark and removing the mucilage by fermentation(de Melo Pereira *et al.,* 2019). The use of wet process is done to avoid phenolic fermentation during the drying process. The most important difference between the dry and wet processing is the removal of the pulp which in the later is done prior to the drying and the fermentation step

which occurs only in the wet process whereas in dry process the pulp is removed post drying (Duarte *et al.*, 2010).

Wet process uses specific equipment and large amounts of water where the pulp is removed by the use of a pulper and the mucilage removed by chemical products or natural fermentation (Duarte *et al.,* 2010). The coffee cherry when harvested and sorted in the field is received in the factory, weighed and put into a tank where they are transported by water rails or conveyer belts into the next step. The initial sorting is done by floatation where a water siphon separator is used. The foreign matter such as leaves and twigs tend to float and are therefore removed although some of the cherries might also float due to their lower densities as a result of various defects. Once sorting is complete, the cherries are transported by gravity and or water through de-pulping machines that are responsible for the removal of the pulp by pressure and or friction. The pulp is removed from the wet mill with an auger or through a water channel and dropped either onto the ground or into a truck to be transported to a different location (Rotta *et al.*, 2021).

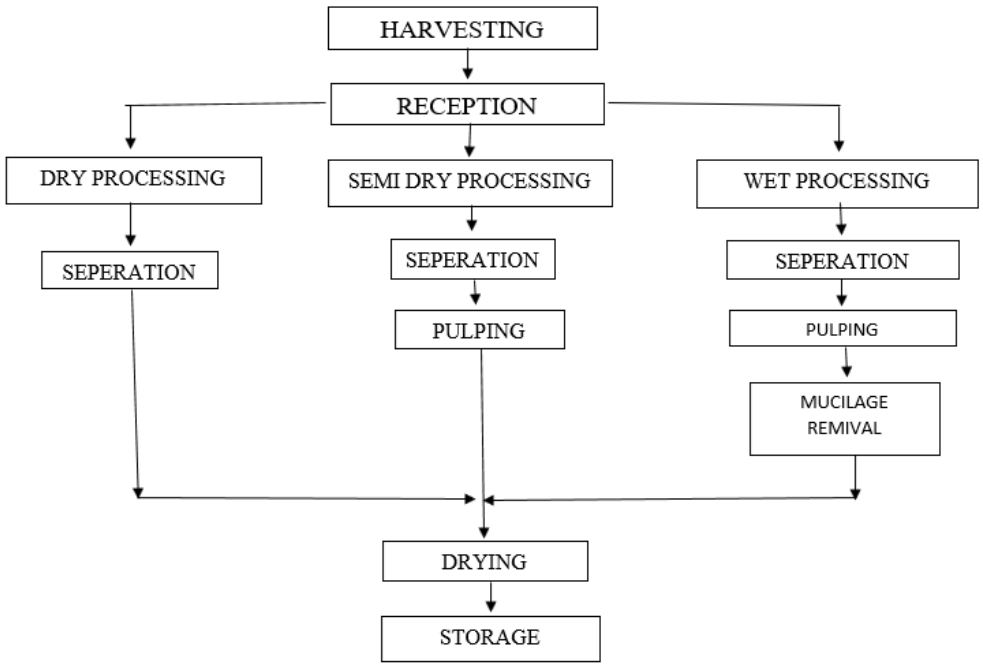

Figure 2.4: The various processing methods of coffee cherries (Wintgens, 2004)

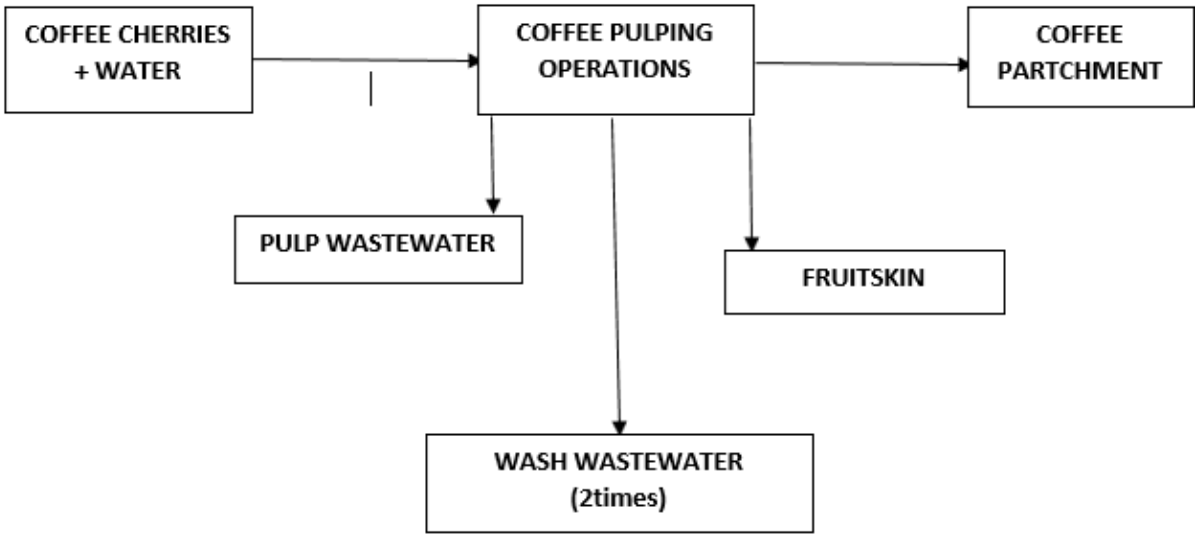

Figure 2.5: Coffee pulping process with various products and by-products (Wintgens, 2004)

2.9.Coffee Pulp

Coffee pulp is the major waste product of the wet processing of the coffee berry and represents 40% of the fresh fruit weight which also means that it accounts for nearly a similar margin for the resultant coffee waste produced (Villa Montoya *et al.*, 2020). The pulp is basically composed of the pericarp or outerskin and the mesocarp. The pulp is made up of carbohydrates, fibers, protein, fat, caffein, tannins and other polyphenolic compounds (da Silveira *et al.*, 2020). Flavanols, flavan-3-ols, hydroxycynamic acids and anthocyanidins classes of polyphenols have been identified in coffee pulp with some of the phenolic compounds identified being epicatechin, catechin, rutin and ferulic acid (da Silveira *et al*., 2020; Tran, 2020).

According to Ramón-Gonçalves *et al.*, (2019) coffee byproducts which include the pulp have in their composition substantial quantities of bioactive components such as polyphenols with several polyphenolic compounds like ellagic, gallic, p-hydroxybenzoic, tannic acids, catechin and epicatechin have been identified. In their study, Lertchunhakiat *et al.*, (2016) quoted that coffee pulp contained 1.5-8% tannins based on dry weight and went ahead to tan

crossbreed boar goat fur skin with coffee pomace. It is with this background that this study focused on the tanning viability of coffee husks and parchment.

2.10. The Tanning Process.

Leather making follows a process that takes time and has chemical components in the process and mechanical operations which are generally classified as processes before tanning, the actual tanning and processes done after the tanning operations (Mengistie *et al.*, 2016; Vijayaraghavan *et al.*, 2015). The various pre-tanning methods are soaking, liming, deliming and bating with tanning operations being pickling and the actual tanning process whereas the post tanning processes are additional tanning process which is also known as retanning, the addition of colour into the leather also known as dyeing and fatliquoring.

The soaking process is the first process of leather manufacturing in which the dehydrated hides and skins due to curing are rehydrated and brought back to a flaccid condition and non-collagenous components of the skin are removed (Ma *et al.,* 2014). This process in many instances is divided into two subprocesses: the dirt soak and the main soak where the first cleaning is meant to remove dirt and unwanted materials attached to the hides and skins (Morera *et al.,* 2013). The first soak is meant to rehydrate the hide or skin in order to ensure that proper cleaning occurs in the second soak while the second soak aims not only to rehydrate the hides or skins but also to open up the fibers, to remove the denatured soluble proteins and the salt from curing (Queiros *et al.*, 2018).

Unhairing, though it is conducted in the same vessel and float with liming, is a completely different process where the epidermis and hair are removed (Yahia *et al.*, 2019). The conventional method employed is the use of lime (also referred to as calcium carbonate) and sodium sulphide. Hydrogen sulphide has been reported to contribute to degradation of the environment. The utilization of enzymes for unhairing especially keratinases has been

suggested and research continues on the same though it has faced various challenges (Sivasubramanian *et al.,* 2008). In the conventional method both liming and unhairing occur simultaneously with the lime aiding to dissolve non-structural proteins i.e. albumins and globulins and adipose tissue, to facilitate opening up through swelling of the hide and skin, to open up the collagen fiber and to partially convert fat or grease into soap for easy removal (Hashem *et al.,* 2016).

The process of degreasing aims to completely remove fats from the skins containing a lot of fat in the skin structure since the fat or grease may result in various defects which may include dyeing that is not even, excessive hexavalent chromium and fat spues (Rosa *et al.,* 2017; V. Sivakumar *et al*., 2009). There are various methods for the removal of fats such as the use of surfactants to emulsify the fat which is a highly effective method, saponification of fats with alkali and the use of organic solvents such as kerosene and dichloromethane to extract and remove oils (Li *et al*., 2020).

The deliming of the pelt involves the use of ammonium salts i.e. ammonium sulphate and ammonium chloride to neutralize the alkali which was introduced in the previous stage of liming (Lei *et al*., 2020). This is achieved by the removal of lime that has been mechanically held and lime that has been chemically bound and converting them into soluble salts(Deng *et al*., 2015) and lowering the pH as a result in preparation for bating. Bating is an important step in leather manufacture because here non collagenous proteins are degraded and collagen fibers separated. This result in pelt becoming soft (Hameed *et al*., 1996). This prepares the collagen fibers for the actual tanning and removes from the pelt any remaining unwanted substance from previous operations by utilizing enzymes. The two operations of deliming and bating are done continuously in the same vessel with the same float where deliming is conducted first then followed by bating operation (Gallego-Molina *et al.,* 2013).

Pickling is an operation that is commonly employed in conventional chrome tanning where the bated pelt is treated with an acid, in the presence of salt (NaCl) to avoid acid swelling of collagen while reaching an equilibrium pH of 2.8-3.0 (Jia *et al.,* 2016).

The aim of the tanning process is to bring physical and chemical changes in the hides and skins by imparting enzymatic and thermal stability of the collagen matrix of hides or skins. This done using tanning agents such as chromium due to its high hydrothermal stability resulting to shrinkage temperatures higher than 110^{o}C Ariram and Madhan, (2020) and vegetable tannins which are able to permanently combine with proteins and therefore inhibit their activity. For vegetable tanning, in the tanning bath, the tannins diffuse into the hide or skin and bond with the collagen where complexation occur resulting in the stabilization of the animal hide (Maier *et al.,* 2017b).

The retanning step in the leather manufacture process reinforces the physical characteristics and improves the mechanical properties of the leather as additional tanning is done by retanning agents (Sun *et al.,* 2018). These agents can be classified as inorganic and organic retanning agents. The inorganic agents are basic chromium, zirconium and aluminum salts whereas organic retanning agents are vegetable tannins, synthetic tanning agents, oil tanning agents and resin tanning agent (Liu *et al.,* 2020).

Dyeing is the application of dyes which are highly colored substances also referred to as colorants to impart color to the substrate i.e. leather (Venkatasubramanian Sivakumar *et al.,* 2009). The leather industry uses three main types of dyes i.e. acid, basic and direct dyes where the acid dyes are normally azo, tri-arylmethane or anthraquinone dyes, the basic dyes have free amino acids while the direct dyes are water soluble salts of sulphonic acids of azo dyes (Krishna Priya *et al.,* 2016). Conventionally, dyeing can be done in a continuous or

batch process which will depend on the type of material and dye bath and the process is conducted in high temperatures (Campardelli *et al*., 2020).

When the tanning is complete, the skin has lost a majority of its natural oils which result in lack of proper lubrication between the fibrils leading to a hard, non-stretchable leather that is difficult to work with. A fatliquor or lubricant composed of non-ionic oil and emulsifier is introduced into the leather and this prevents the sticking together of fibers (Nkwor and Ukoha, 2020).

CHAPTER 3. MATERIALS AND METHODS

3.1. Sampling area

The samples were collected from Yadini farm, Kiambu County. Kiambu county has a low altitude of 1520 m and a high altitude of 1820m. The county is located between latitudes 00 25’ and 10 20’ south of the Equator and Longitude 360 31’ and 370 15’ East of the Equator. Kiambu county has three types of soils; high level uplands which mainly comprises volcanic soils, plateau soils which comprise low fertility clay and sandy soils and volcanic footbridges soils. These soils are very fertile which makes them to be useful for both livestock rearing and crop growing i.e., cash crops and food crops. Coffee is mainly grown in Juja, Thika town, Ruiru and Lari constituencies which have volcanic soils. Samples for the research were taken from Kahawa bora coffee mills located within the premises of Yadini farm.

Figure 3.1: A Map of Kiambu county and its constituencies

3.2. Sample Selection and Preparation

The study had a purposive sampling design with the coffee pulp samples gotten from Kahawa Bora coffee mills in Yadini farm. Fresh coffee pulp and old pulp from the factory was obtained at the coffee pulp dumping site and was wet by nature of the water used in the de-pulping process and transportation to the site. The fresh pulp was identified by their red and yellow colour while the old coffee pulp was identified by their black colour. Twelve samples were collected each weighing ten kilograms and air dried until constant weight was achieved. The samples were collected randomly from three different points in four different days.

Plate 3.1: Drying of *Coffea arabica* Pulp.

Plate 3.2 Dried coffee arabica pulp

Table 3.1: Water loss by weight in coffee pulp samples

Sample	Day 1	Day 2	Day 3	Day 4	Day 5	Final percentage weight loss
S1	87.39	43.91	23.62	21.83	21.83	75.02
S2	90.41	47.69	32.51	28.92	28.92	78.61
S3	102.62	57.47	28.74	19.48	19.48	81.02
S4	83.26	41.63	24.15	17.33	17.33	79.18
S5	75.45	40.74	22.65	14.68	14.68	80.54
S6	88.98	36.48	25.85	17.20	17.20	80.67
S7	93.20	50.33	27.03	17.78	17.78	80.92
S8	79.25	40.99	22.98	14.14	14.14	82.16
S9	92.11	47.89	28.55	20.63	20.63	77.60
S10	65.36	34.64	18.95	12.41	12.41	81.01
S11	72.84	40.06	23.30	13.85	13.85	80.95
S12	97.39	47.71	28.24	18.54	18.54	81.00

Once the wet coffee pulp reached a constant weight, the dry coffee pulp was taken to the Department of animal production and nutrition where they were ground by a star mill. The weight loss observed in all the samples indicated that 75-82% of wet weight was due to the presence of water.

Plate 3.3: Ground coffee arabica pulp

3.3.Test for Tannins

One gram of ground coffee pulp and mimosa were each poured into a 100ml beaker and 10 ml of distilled water added to each beaker. The sample together with the distilled water were heated to boiling point and left to boil for five minutes. The liquid was then filtered from the solids and 2ml of the filtrate put in a test tube. A few drops of 10% ferric chloride were added to the solution where an observation of a blue black or green solution was indicative that tannins are present (Yisa, 2009).

3.4.Test for Condensed and Hydrolysable Tannins

The individual solutions from the test of tannins (Section 3.3 above) were mixed with a few drops of aqueous potassium hydroxide. Appearance of a red colour confirmed presence of condensed tannins whereas no observable change confirmed the presence of hydrolysable tannins (Thorstensen, 1993).

3.5.Test for the Tanning Strength of Vegetable Tannins

The hide powder method was employed where the total tannin content was gotten by subtracting total non-tans from total soluble solids. The moisture content, total solids, total soluble solids and pH were also determined as discussed in the sections below.

3.5.1. Hide Powder Preparation

The hide powder was prepared from a bovine hide. The green hide was soaked in salt water and then in fresh distilled water. The conventional unhairing, liming, deliming, bating and pickling were carried out as described by Cabeza et al., (1998). The pelt was then cut into small pieces and ground to powder by a star mill.

3.5.2. Chrome Hide Powder Preparation.

The chrome hide powder was prepared using the official method as described by the Indian standards (BIS, 2013).

3.5.3. Determination of Moisture and Total Solids

Three grams of finely ground coffee arabica pulp sample was weighed on an analytical balance and put in a weighing bottle after which it was heated in an oven at 100^{o}C for 3-4 hours. It was then cooled in a desiccator for 20 minutes and then weighed. The process of heating and cooling was repeated on the same coffee pulp sample until the weight of the sample remained the same or the change in weight after one hour was less than 2mg (BIS 2013).

$$The\ moisture\ content\ percentage\ by\ weight = \frac{(w1 - w2)\ x100}{w2}$$

$$Total\ solids\ percentage\ by\ weight = \frac{w2}{w1}\ X\ 100$$

Where w1- weight in g of the material taken for the test

w2- weight in g of the residue left after drying

3.5.4. Determination of Total Soluble Solids

Two liters of solution was extracted through proctor extraction from a known amount of ground coffee pulp with water as a solvent. Before extraction was started, the tanning material was first soaked in cold water in the extraction chamber and left overnight. The following morning, extraction was started at 40^{o}C with 150 ml of extract collected. The temperature was then raised to 50^{o}c and a further 750 ml collected. The temperature was then gradually raised to 100^{o}C in-order to enhance the extraction process and raise the total yield of extract to 2 liters. The extracted solution was then cooled by immersion into water in a sink at 25±2^{o}C with the flask containing solution agitated from time to time to avoid localized cooling.

The extract (100 ml) was mixed with 1g of kaolin and the mixture transferred to a fluted filter paper (whatmann No. 11). The filtrate was collected in a fresh beaker when filtrate it was optically clear. 50 ml of the filtrate at 27±2^{o}C was pipetted in a porcelain basin and left to dry by evaporation after which the weight of the dry matter was determined (BIS, 2013). The test was conducted in duplicates and the total soluble solids determined as follows:

$$Total\ solubles\ percentage\ by\ weight = \frac{w2}{w1} x \frac{v1}{v2} x\ 100$$

Where w2-weight in grams of the residue left after drying.

v1- volume in ml made up originally

w1-weight in grams of tanning material taken

v2-volume in ml of the test solution pipetted out.

3.5.5. Preparation of Chrome Alum Solution

Chromium potassium sulphate (30g) was dissolved in distilled water at room temperature and the solution made to one liter in preparation for the determination of non-tans (BIS, 2013).

3.5.6. Preparation of Gelatin Reagent

Photographic grade gelatin (1g) and 10g of pure sodium chloride was dissolved in 100ml of distilled water at 27^{o}C and pH was adjusted to 4.7 (BIS, 2013). This was done in preparation for the determination of non-tans.

3.5.7. Determination of Non-tannins

A quantity of wet hide powder containing 6.25g of dry hide powder was weighed and added into 100ml of unfiltered tannin infusion and 20ml of distilled water was also added in a wide mouth flask of 300ml capacity. The mouth of the flask was stoppered tightly and shaken with great vigour by hand for 15 seconds and then taken to a mechanical rotary shaker where it was shaken for 10 minutes at 50 to 65 revolutions per minute. The powder and the solution were poured on a clean dry linen filter cloth supported by a funnel and was drained and squeezed by hand. Kaolin (1g) was added to the filtrate and poured into a single 15cm pleated filter paper returning the filtrate until it is clear. The filtrate was tested with gelatin salt reagent for turbidity and 50 ml of it evaporated in a tared porcelain to give a residue that was dried in a vacuum oven at 98-100 ^{o}C with repeated cooling and weighing until a constant weight was obtained. The residue weight obtained was multiplied by a factor of 1.2 to correct the 20 ml of water of dilution introduced by the wet hide powder into the 100 ml of tannin solution (BIS, 2013).

$$Non - tannins\ percentage\ by\ weight = \frac{w2\ x\ v1}{w1\ x\ v2} x100$$

Where w2-weight in grams of the residue left after drying

v1-volume in ml made up originally

w1-weight in grams of material taken

v2-volume in ml of the test solution taken.

3.5.8. Determination of Tannins

The tannins were determined by subtracting the total non-tannins from the total soluble solids (BIS, 2013).

$$tannins\ percentage\ by\ weight = x - y$$

Where x- total soluble percentage by weight

y-non tannins percentage by weight

3.5.9. Determination of Alkalinity and Acidity

The alkalinity of the solution of *C. arabica* pulp prepared was determined by adjusting the relative density to 1.5g/ml at 27 ^{o}C with cold water by use of a pH meter (BIS, 2013).

3.6.Tanning

The coffee pulp obtained from the factory was dried and ground into powder using a mill where particles with less than 2mm were used for tanning. The processes before and after the actual tanning process were similar for both the coffee pulp tanning procedure and commercial mimosa which was used as a standard. Ten wet salted goatskins were used with five used for coffee pulp and the remaining five for commercial mimosa tanning. The process recipe used is attached in Appendix 2.

3.7.Comparison of Physical Properties of Coffee Pulp and Mimosa tanned leathers

The leathers tanned with *C. arabica* pulp and mimosa were passed through various functionality tests to determine their quality. These physical tests included measurement of shrinkage temperature, tear load, tensile strength, flexing endurance and resistance to grain cracking.

3.7.1. Sampling and Conditioning.

Samples were taken from each side of the goatskins according to the method prescribed by IUP 2 method. (IULTCS, 2001).

The test pieces were kept in standard atmosphere 20/65, i.e., 20± 2 ^{o}C temperature and 65±5% relative humidity for 48 hours as prescribed in the official method (IUP 3, 2001).

3.7.2. Shrinkage Temperature

The measurement of the shrinkage temperature for mimosa and *C. arabica* pulp tanned goatskins was carried out using the SATRA STD 114 test equipment following the official test methods (IUP 16, 2001). Leather strips were cut measuring 50 mm x 2 mm from the vegetable tanned goatskins. The specimens were cut parallel and normal to the backbone. Holes were punched on the ends of the leather specimen to allow the sample to be suspended vertically in the test chamber filled with water and a small load attached to the lower end. An adjustable marker placed on the outside of the tube was used to indicate the position of the lower end to help note when shrinkage occurred. The equipment was then closed and water was heated at a rate 4^{o}C/min by application of external heat to the boiler components. The temperature at which the leather began to shrink was taken as the shrinkage temperature.

3.7.3. Flexing Endurance

The measurement of flex resistance was carried out by use of a bally flexometer as described by IUP 20 of physical testing methods. The leather sample cut with the dimensions 70mm x 45mm were folded and fixed to the jaws of the instrument in such a way that the grain side remained outside with fold on the sample. The instrument was then switched on and the flexing done on the leather samples when folded until 100000 cycles and observations made periodically for any crack signs on the surface of the leather.

3.7.4. Tear Load

The tear strength of the tanned goatskins was measured by the use of Instron 1011 in line with the official test method (IUP 8, 2001). Six pieces of leather test specimens were cut as a rectangle with dimensions 50mm long and 25 mm wide using a press knife which cuts out the specimen and slot in one operation parallel and perpendicular to each position. Three test pieces were cut parallel to the backbone with the remaining cut in a perpendicular direction. The Instron 1011 machine was used because it had a uniform speed of jaw separation with the rate of 100mm per minute used and the readings of the load fall in that part of the scale which was shown by calibration to be correct within 1%. The machine was run once the specimen were clamped on the jaws until the specimen was torn apart with the highest load reached recorded as the tear load. The tear load was recorded in Newtons.

3.7.5. Resistance to Grain Cracking

The ball burst test otherwise known as resistance to grain cracking was conducted using a lastometer STD 4 in line with the physical test method IUP 9 (IUCLTCS, 2001). The test piece leather was disc shape and was held down firmly by clamping rings with a spherical underneath with its tip just touching the flesh surface. The specimen was moved downwards against the rod, distending the grain of the leather above the rod immediately with the surface

watched for first signs of cracking and bursting. Upon cracking and bursting of the grain, the force and distention values at the individual points were observed and recorded.

3.7.6. Tensile Strength

The tensile strength was determined using Instron 1011, in line with the official test method (IUP 6, 2001). Six samples were cut by use of a dumb-bell shaped press knife with the three samples being parallel and the other three perpendicular to the backbone. The jaw of the machine was set at 50 mm apart and the test piece was clamped into the jaws with the jaws lying along the midline. The machine was run until the sample broke and the highest value of the load observed taken as the breaking load. Tensile strength was recorded in newton per cross sectional area.

The elongation at break was recorded together with the tensile strength by the machine and as such the values recorded were given as a percentage of 50mm.

3.8.DATA ANALYSIS

The data from *C. arabica* pulp that was collected was subjected to analysis by descriptive statistics. This was done using the general statistics (GENSTAT) software with a t test done for comparison. The means for shrinkage temperature, flexing endurance, tear load, resistance to grain cracking and tensile for the leathers tanned with tannins from *C. arabica* pulp were compared with those from mimosa tanned leathers. The level of significance was tested by the use of a student t statistic with a p value of less than 0.05 indicating that there was a significant difference between the means for *C. arabica* tanned leather and mimosa tanned leather.

CHAPTER 4. RESULTS

4.1. Test for Presence and Type of Tannins

The test for presence and type of tannins in *C. arabica* pulp showed that the pulp contains condensed tannins. This is because the solution first changed to a green colour upon the addition of ferric chloride (iron III chloride/iron trichloride) and later changed to a reddish brown colour upon the addition of potassium hydroxide to the same solution that had been mixed with ferric chloride. All the 12 samples tested positive for presence of tannins and for condensed tannins.

Table 4.1 Phytochemical Test Results for *Coffea arabica* Pulp and Mimosa

Phytochemical	Test Procedure	*C. Arabica* Pulp	Mimosa
Tannins	Ferric chloride test	+	+
Hydrolysable tannins	Potassium hydroxide test	_	_
Condensed tannins	Potassium hydroxide test	+	+

KEY

+ →Presence of Phytochemical

- →Absence of Phytochemical

4.2. Analysis of Tannin Content and Tanning strength of *Coffea arabica* pulp

The tanning content for coffee pulp was found to be 5.23% with a tanning strength of 2.43 as compared to that of mimosa being used as a positive control which was 64% and 2.9 respectively. The tanning strength was obtained as a function of the tannins and soluble non-tannins calculated by dividing the tans by the non-tans. The pH of *C. arabica* pulp was 4.7 while that of mimosa was 4.6.

The results for moisture content, total solids, total soluble solids, soluble non tans, tannins and pH were as follows:

Table 4.2: Results for Tanning Strength, Tannins and Non-tans of *Coffee arabica* pulp samples

Properties	S1 old	S2 f	S3 f	S4 f	S5 old	S6 f	S7 f	S8 f	S9 f	S10 f	S11 old	S12 f
Moisture content	10.81	10.53	10.32	9.64	11.21	10.12	11.14	10.92	8.51	9.81	10.01	10.74
Total solids	89.19	89.47	89.68	90.36	88.79	89.88	88.86	89.08	91.49	90.19	89.99	89.26
Soluble solids	6.84	7.69	7.45	7.13	6.53	7.39	7.01	7.41	7.85	6.97	7.73	7.30
Soluble nontans	2.06	2.58	2.29	2.12	1.88	2.35	1.94	2.28	2.67	2.04	2.50	2.21
Tannins	4.77	5.11	5.16	5.01	4.65	5.04	5.07	5.13	5.18	4.93	5.23	5.09
Tanning strength	2.31	1.98	2.25	2.36	2.47	1.94	2.59	2.25	1.94	2.41	2.09	2.30
pH	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7

KEY

S → Sample

Old → Coffee pulp that had stayed in dumpsite for more than one week

f → Coffee pulp that had stayed in the dumpsite for less than one day

Table 4.3: Summary of Tanning strength, Tannins and Non-tans of *Coffea arabica* and Mimosa

Properties	Coffee Pulp	Mimosa
Moisture content %	10.31	8.05
Total solids %	89.69	91.95
Total Soluble solids %	7.28	86.04
Soluble Non-tans (NT) %	2.24	22.54
Tannins (T)%	5.04	63.56
Tanning strength (T/NT)	2.26	2.82
Type of tannin	Condensed	Condensed
pH	4.7	4.6

Table 4.4: P-Values for Moisture, Total solids, Soluble solids, Non tans, Tannins and Tanning Strength.

Properties tested	**P-values**
Moisture	0.001
Total soluble solids	0.001
Soluble non tans	0.001
Tannins	0.001
Tanning strength	0.001

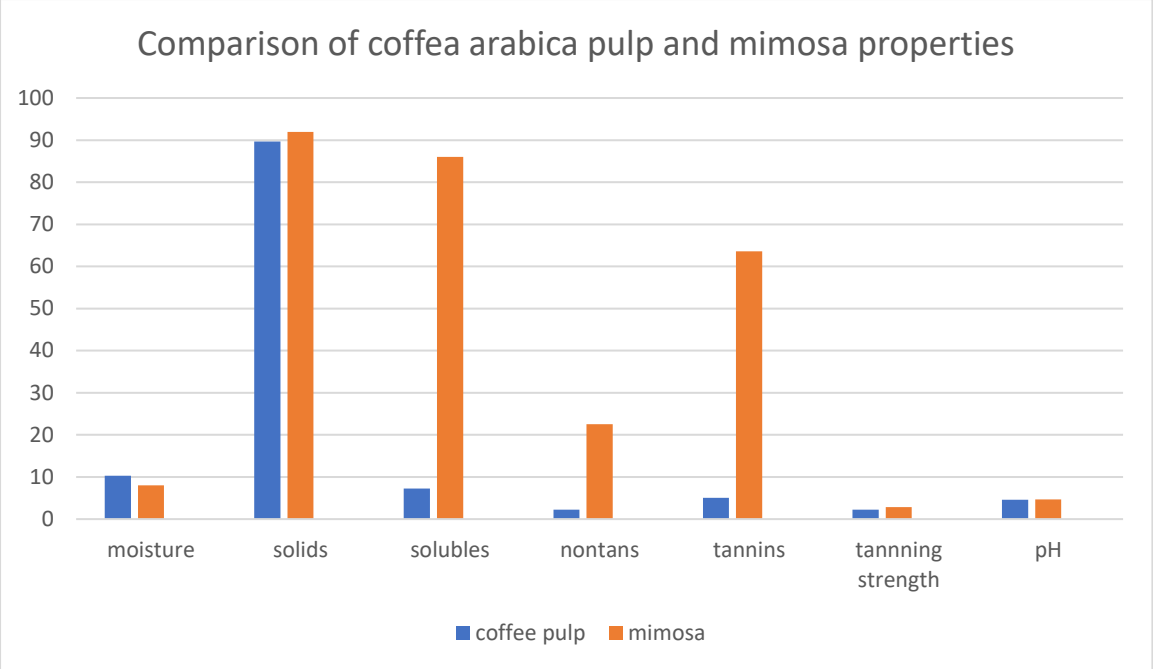

Figure 4.1: Variations in Components of different Tanning materials.

The colour of the coffee pulp changed from red/yellow when wet to black when dry. This can be attributed to the polyphenols undergoing oxidation when drying because of their phenolic structure which makes their oxidation possible(Krishnamoorthy et al., 2014; Tran, 2020)

4.3.Physical Characteristics of *Coffea arabica* and Mimosa Tanned Leathers.

The physical characteristics of leather tended to vary with the type of tannage that is used with different tanning materials producing distinct leathers. The goatskins tanned leathers had different colours for the *C. arabica* pulp tannins and the commercial mimosa. The wet *C. arabica* pulp tannins had a brown colour with the mimosa having a red shade.

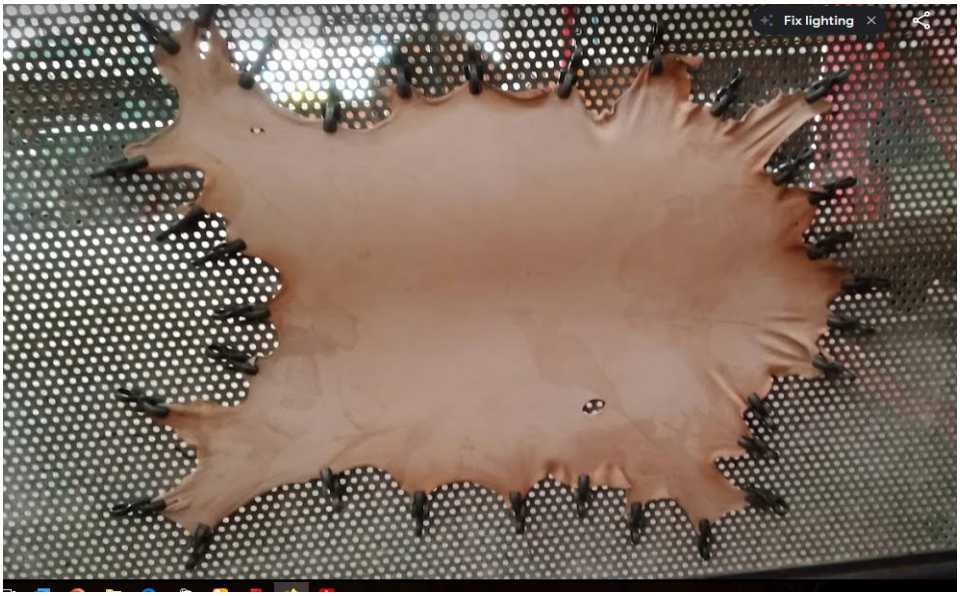

Plate 4.1: Brown dry Mimosa Tanned Leather being Toggled.

Plate 4.2: A Dark brown coloured *Coffea arabica* Tanned Leather.

4.3.1. The Shrinkage Temperature

The shrinkage temperature is used as a measure of hydrothermal stability of the tanned leather and in result indicating the level of tannage that occurs. The test was conducted after tanning with the *C. arabica* pulp leather having a shrinkage temperature of 62ºC whereas that of Mimosa was observed to be 83ºC. It is of importance to note that tanning using coffee pulp was not complete as the penetration was not complete. This was despite the addition of more

tanning materials. The test was however conducted in duplicates to ensure reproducibility. Table 4.5 below shows the shrinkage temperature of the two tanning agents.

Table 4.5: Shrinkage Temperature of *Coffea arabica* pulp and Mimosa Tanned Leathers.

Tannins	No. of samples	Shrinkage temperature
Coffee pulp	16	62
Mimosa	16	83

4.3.2. Tensile Strength and Elongation

The tensile strength of leather is the ability of leather to withstand stress without breaking i.e., the stress at which the leather will fracture whereas elongation of leather is the ability of leather to stretch before fracture occurs. Tensile strength is dependent on the cross-sectional area of leather. The tensile strength was determined on samples collected from both the parallel and perpendicular directions to the backbone. The measurements recorded a maximum of 17.87 N/mm^2 and a minimum of 11.40 N/mm^2 parallel to the backbone and a maximum of 21.40 N/mm^2 and a minimum of 16.3 N/mm^2 perpendicular to the backbone for *C. arabica* pulp tanned leather. This was in contrast to mimosa with a maximum of 27.4 N/mm^2 and a minimum of 21.00 N/mm^2 parallel to the backbone and a maximum of 30.75 N/mm^2 and a minimum of 24.6 N/mm^2 perpendicular to the backbone. The tensile strength for coffee pulp leather was significantly different from leather tanned with mimosa ($p<0.001$).

Table 4.6: Tensile strength and Elongation of *Coffea arabica* pulp and Mimosa Tanned Leathers.

Tanning Material	Fiber run	Average thickness	Average tensile Strength	Percentage average elongation
C. arabica pulp	↑	0.72±0.07	14.72±2.03	14.44±2.22
C. arabica pulp	→	0.85±0.07	19.09±1.60	9.89±1.18
Mimosa	↑	1.36±0.20	24.19±2.25	45.74±1.40
Mimosa	→	1.33±0.08	27.21±3.26	41.92±2.36

Key

↑ - parallel to the backbone

→ - perpendicular to the backbone

4.3.3. Tear Strength

The tear strength of leather is its ability to withstand applied forced in a specified direction before tearing or making a cut. *C. arabica* pulp tanned leather had its highest tear strength recorded as 50.50 N/mm^2 and the lowest being 30.87 N/mm^2 perpendicular to the backbone and a high of 72.12 N/mm^2 and a low of 54.00 N/mm^2 parallel to the backbone. Mimosa tanned leather on the other hand recorded tear strength of 86.50 N/mm^2 high and a low of 64.25 N/mm^2 perpendicular to the backbone and a high of 94.37 N/mm^2 and a low of 77.62 N/mm^2 parallel to the backbone.

Table 4.7: Tear Strength of *Coffea arabica* pulp and Mimosa Tanned Leathers.

Tanning material	Fiber run	Average thickness	Average tear strength
C. arabica pulp	↑	0.72	48.00±14.15
C. arabica pulp	→	0.85	38.12±3.13
Mimosa	↑	1.45	75.97±8.68
Mimosa	→	1.32	72.08±8.19

Key

↑ - Parallel to the backbone

→ - Perpendicular to the backbone.

4.3.4. Grain Crack and Grain Burst

The grain crack and grain burst were measured by the use of a lastometer. The highest value recorded for *C. arabica* pulp leather was a grain crack of 5.89 with a corresponding grain burst of 6.99 with the lowest values for the grain crack and corresponding grain burst being 3.77 and 5.07 respectively. The highest values for mimosa tanned leather were 7.74 for grain crack and 8.67 for grain burst with the lowest values for grain crack and grain burst being 7.16 and 8.03 respectively. Mimosa tanned leather had the highest grain crack and grain burst as compared to *C. arabica* pulp leather. The results showed a significant difference $p<0.05$ for the ball burst of mimosa and coffee pulp leathers.

Table 4.8: Ball Burst test results for *Coffea arabica* pulp and Mimosa Tanned Leathers.

Sample	Average Grain Crack	Average Grain Burst
C. arabica pulp	4.52±0.31mm	5.93±0.28mm
Mimosa	7.47±0.09mm	8.25±0.15mm

4.3.5. Flexing Endurance

Flex endurance test is used to measure the number of times a material undergoes the flexing action without cracks appearing. The bally flexometer was used to measure the flex endurance for *C. arabica* pulp and mimosa tanned leather. In regards to mimosa tanned leather, there was no visible damage or cracks at 100000 flexes for the samples which were taken parallel ↑ and perpendicular → to the backbone. However, for *C. arabica* pulp tanned leather there were visible cracks or damage to the leather at 50000 flexes for both the samples parallel and perpendicular to the backbone.

Table 4.9: Physical Characteristics of *Coffea arabica* and Mimosa Tanned Leathers.

Physical Properties		***C. arabica* pulp**	**Mimosa**	**Minimum recommended value**
Ball Burst Distention	Grain Crack	4.52±0.31mm	7.47±0.09mm	6.5
	Grain Burst	5.93±0.28mm	8.25±0.15mm	7.0
Shrinkage temperature		62^{o}C	83^{o}C	70
Thickness (mm)		↑ 0.72±0.07	↑ 1.36±0.20	>0.5
		→0.85±0.07	→ 1.33±0.08	
Tensile strength		↑14.72±2.04	↑24.19±2.25	>12
		→19.09±1.60	→27.20±3.26	
Elongation at break		↑14.44±2.22	↑45.74±1.40	>40
		→9.89±1.18	→41.92±2.36	
Flexing endurance		↑ Cracks visible @ 10000 flexes	↑ No damage @ 100000 flexes	No damage @ 100000 flexes
		→ Cracks visible @ 10000 flexes	→ No damage @ 100000 flexes	
Tear strength		↑48.00±14.15	↑75.97±8.68	>20
		→38.12±3.13	→72.08±8.19	

Key

↑ → samples cut parallel to the backbone.

→ → samples cut perpendicularly to the backbone.

Table 4.10: P-values of physical characteristics of *Coffea arabica* and Mimosa tanned leathers

Physical Properties	**p-value**
Ball burst	0.001
Shrinkage temperature	0.001
Thickness	0.001
Tensile strength	0.001
Elongation at break	0.001
Flexing endurance	0.001
Tear strength	0.001

CHAPTER 5. DISCUSSION, CONCLUSIONS AND RECCOMENDATIONS

5.1. Presence and Type of Tannins

The study showed that *C. arabica* pulp in Yadini farm, Kiambu county contained tannins as a green colouration was observed when reacted with ferric chloride (iron (III) chloride). The class of tannins detected was condensed tannins as the extract readily formed a red colour upon the addition of potassium hydroxide. This was in agreement to a study by Wong-Paz *et al.,* (2021) where their extract from *C. arabica* pulp with aqueous acetone contained condensed tannins. A study in Thailand by Rakitikul, (2017) on *C. arabica* pulp also identified the condensed tannins as the type of tannin present in the pulp. The condensed tannins are preferred for vegetable tanning as they provide more sites for bonding at the 5- and 7- positions where the quinoid species form covalent bonds with lysine. This bonding ensures that breaking of hydrogen bonds for condensed vegetable tanned leathers does not return the leather to raw hide or skin (Covington, 2009).

5.2. Analysis of Tannin Content and Tanning Strength

The average tannin content of *C. arabica* pulp obtained from Yadini farm was found to be 5.04% with that of mimosa being 64%. The student t-test showed that there was a significant difference between *C. arabica* tannins and mimosa ($p<0.001$). *C. arabica* pulp which had remained at the dumpsite for a longer period of time by the time of sampling had a lower tannin content as compared to fresh coffee pulp. This could be due to the fact that water is able to remove phytochemicals from the pulp when left in contact for a prolonged time. The processing of coffee ensures that the coffee pulp is left in a wet condition with approximately 80% of its composition being water. When the pulp is discarded to the dumpsite, the water tends to slowly move from top to bottom and eventually drains away. It is in this process that some of the phytochemicals including tannins are removed from the pulp. The results of this study were in agreement with previous studies with Murthy and Naidu, (2012) indicating that

the tannin content of coffee pulp is at a range of 1.8 to 8.56%. A similar study by Rakitikul, (2017) in Thailand gave the tanning content of coffee pulp at 5.68% which was closer to the results obtained in this study. The slight differences in the tanning content of the pulp could have been due to the different environmental factors, with there being variations between the temperatures in Kenya and Thailand. Other environmental factors such as the amount of water present and the type of soil where the plant was grown could have contributed to these slight differences. It is important to note that the extraction process that resulted in the said tannins in this study began at 40^{o}C and was completed at 100^{o}C. The high temperatures were used in order to yield the highest possible amount of tannins and also reduce or eliminate the amount of undesirable compounds like gums which introduce undesirable characteristics to the leather (China *et al.,* 2020a).

The tanning strength for *C. arabica* pulp was 2.26. with the tanning strength obtained by dividing the tannins by the non-tans. This was in comparison to mimosa which had a tanning strength of 2.82 with both the tannins exceeding the required minimum of 0.5 (Kuria *et al.,* 2015) with the tanning strength obtained by dividing the amount of tannins with the amount of non-tans, the non-tans as a result play an important role in the tanning process. As earlier stated in literature, the non-tans aid in the penetration of the tannins into the pelt. However, when the amount of non-tans exceeds the amount of tannins, the tanning strength is reduced which then lowers the ability of the tanning material to convert the pelt into leather.

There was a significant difference ($p<0.05$) between the tanning strength of *C. arabica* pulp and mimosa. There was no literature found on the tanning strength of coffee pulp whereas several studies were obtained for mimosa tanning strength. A study in Kenya by (Kimaiga, 2016) on plectanthrus barbatus, established the tanning strength of mimosa to be 2.8.

The pH of *C. arabica* pulp extract was 4.7 whereas that for mimosa was recorded as 4.6. which are in-line with the recommended pH of 4 to 6. This is because for pH less than 4 the pelt tends to react with the tannins at a higher rate and as a result lead to surface tanning whereas the inside of the pelt remains untanned. This phenomenon is described as case hardening and is not required as it negatively alters the physical properties and quality of leather produced. Condensed tannins in very acidic conditions also tend to aggregate and form larger molecules and therefore inhibiting penetration into the pelt (Reeds, 1969).

5.3.Vegetable Tanning with *Coffea arabica* pulp and Mimosa

The tanning step involved the use of different concentrations of the tanning material with the one kilogram of crude material used in the beginning of the process. There was a continuous increment of the tanning material until 10 % of tannins from the *C. arabica* pulp was used. However, there wasn't any penetration into the fiber structure whereas the surface of the pelt was completely tanned as observed by the brown colour of the surface. Addition of more tanning material did not cause any change in regards to penetration which led to the conclusion that surface tannage had occurred. The pH at the initial stage of tanning was recorded as 6 and dropped continuously until it was at 4.7. There are several possibilities in regards to the surface fixation of the *C. arabica* pulp tannins to the surface. The first possibility which might have caused the phenomenon would have been due to the high affinity of the tannins to the collagen in the pelt due to the tannins being highly astringent. In regards to astringency, not only could the phenomenon be caused by the tannins themselves, but it could have been caused by the presence of gums which are extracted together with the tannins at high temperatures which are meant to increase the tanning yield (Covington, 2009).

The second possible explanation for the lack of penetration of the tannins would be due to their molecular size. This is because for tannins to penetrate into the leather, not only is their astringency supposed to be low enough, but the molecular size should be small enough to

penetrate through the interfibliary spaces. This means that there is a possibility that the *C. arabica* pulp tannins have a large molecule size and thus only reacted with the surface. These possibilities were however not studied as they were outside the scope of this study but further studies are recommended in order to identify the reason which resulted in surface tanning and lack of penetration.

The final possibility which could have contributed to the case hardening as surface fixation or tanning is commonly regarded, as a case where the non-tannins far out-weigh the tannins. However as clearly demonstrated by the study, the tannins non-tans relation for this study was well balanced with the tannins being more than the non-tans.

5.4.Physical Properties of the Tanned Leather

One of the physical characteristics of the tanned leathers that was conspicuous was the change of colour of the leathers in the wet and dry conditions. The *C. arabica* pulp leather changed from a brown to dark brown upon drying with mimosa changing from reddish brown to light brown. When wetting back was done, the colour of the *C. arabica* pulp leather reverted back to the brown colour.

The colour of vegetable tanned leather is brown, yellow or supple with the exact colour being defined by other factors such as the colour of the skin used and the chemicals which were used for processing(Krishnamoorthy *et al.*, 2014). Various established tannins used in the leather industry produce leathers with these colours with oak tanned leather being yellow in colour, mimosa producing pink and sumac being cream with the differing colours being attributed to differences in structures of the individual tannins (Redwood, 2020).

The tannins found in both *C. arabica* pulp and mimosa were condensed tannins and they have a polyphenolic structure and just like other polyphenols are able to scavenge oxygen and hydroxyl radicals through electron donation (Jiang *et al.*, 2020). This is the reason why

condensed tannins are considered to have antioxidant activities although differing from plant to plant due to various differences recorded in literature. The drying of leather means that the water present is converted from liquid to gas and as such the interaction between the tannins and water is broken allowing the leather to come into contact with oxygen and form new bonds to stabilize the structure. When vegetable leathers are exposed to non-oxidative conditions, they tend to form non-covalent bonds whereas when the oxidative conditions are met, they form covalent bonds. It is this change in structure that leads to the change in colour of the vegetable tanned leathers (Krishnamoorthy *et al.*, 2014).

5.4.1. Shrinkage Temperature

The shrinkage temperature in leather tanning is an important parameter as it not only indicates the level of tanning but also the quality of the leather. This measures the hydrothermal stability of the tanned material. The formation of crosslinking bonds between collagen and the tanning agent plays an important role in determining the shrinkage temperature. This is because when these bonds are formed, the solubility of collagen is reduced and in result the shrinkage temperature of the resultant leather will be increased(Valeika and Širvaityt, 2010). The formation of these crosslinking bonds highly depends on the tanning material being used as different tanning agents produce different quantities of these bonds with collagen. It therefore means that for a tanning agent which is able to form a greater number of crosslinking bonds, the shrinkage temperature will be higher whereas those that forms minimal numbers of bonds, the shrinkage temperature will be lower and as such determining the level of tannage. Just like the term shrinkage temperature implies, it is the temperature at which the tanned material will begin to shrink and is used to determine the thermal stability of the tanned material.

The shrinkage temperature of *C. arabica* pulp tanned leather was observed to be 62^{o}C while that for mimosa was observed to be 83^{o}C. It was no surprise for that the observed shrinkage

temperature for the two materials were observed to be such. This is because in regards to *C. arabica* pulp leather, penetration wasn't achieved as required and as such the formation of crosslinking bonds was not achieved in the pelt. For the formation of these bonds, the *C. arabica* pulp tannins were required to be present in the pelt in-order to interact with the collagen. However, for the mimosa tannins, penetration was completely achieved and as a result of crosslinking bonds were formed and as such the relatively high shrinkage temperature was observed. Leathers that have been properly tanned normally have their shrinkage temperature above 70^{o}C which means that the *C. arabica* pulp tanned leathers were unable to achieve complete tanning.

5.4.2. Tensile Strength and Elongation

The test for the tensile strength of leather in the leather industry is used routinely to determine the quality of the leather and as such is an important parameter. The test is conducted by applying stress in a longitudinal direction until the leather reaches the breaking point. The tensile strength in one specific piece of leather is not the same across the surface of the leather. It changes with change in the direction of stress where the tensile strength of a piece of leather parallel to the backbone is not equal to the one perpendicular to the backbone. It is worth noting that the tensile strength is greatest near the backbone and gradually reduces as you move away from the backbone to the bellies(Mete *et al.*, 2014). The tensile strength values are determined by not just the strength of the individual fibers but rather by all the fibers collectively.

The tensile strength of the *C. arabica* pulp leather was significantly different ($p<0.001$) from that of mimosa leather. The tensile strength for both *C. arabica* pulp and mimosa was greater parallel to the backbone as compared to perpendicular to the backbone with values being $\rightarrow$19.09±1.60 N/mm^2 and $\uparrow$14.44±2.22 N/mm^2 for coffee and $\rightarrow$27.20±3.26N/mm^2 and

↑24.19±2.25 N/mm^2 for mimosa. This was in agreement with studies done elsewhere, an example being a study by Kanuri *et al.,* (2019) on the properties of rabbit skins tanned by different tanning materials where the tensile strength perpendicular was slightly higher than that parallel to the backbone. The fibers which are parallel to the backbone tend to have less damage caused by friction hence the higher tensile strength. Although the tensile strength of the *C. arabica* pulp leather was less than that of mimosa, it still was more than the recommended value of 12.

The elongation at break of the leather is directly related to the tensile strength as it is measured alongside it. Elongations refers to the ability of the leather to stretch and is important in the lasting of shoes and also in the making of garment leathers (Kuria, 2015). Even in regards to most leather products, elongations determines whether the product will maintain or lose its shape (Ali *et al.,* 2020). The minimal recommended value for elongation is specific to the end use with leathers for shoe upper requiring an elongation of 30-40%. The elongation for *C. arabica* pulp leather failed to meet this value as it had a mean elongation of 12% while that for mimosa exceeded this with a mean elongation of 44%. This means that the coffee arabica pulp leather was very stiff while mimosa was flexible as those material with very low values for elongation with the flexibility of materials increasing as the elongation increases (Ali *et al.,* 2020). There wasn't any data on the elongation of goatskins tanned by coffee pulp. However, a study by Ali *et al.,* (2020) in Bangladesh found out that tanned goatskin leather had a mean elongation of 47%. This figure may vary depending on various properly tanned goatskin leathers depending on the origin of the animal, the breed, type of tannage and other environmental factors.

5.4.3. Tear Strength

The tear strength measures how a material is able to resist the propagation of cuts under tension. This test is carried in order to determine the fiber strength of the tanned materials since the rupturing only affects a few fibers (Faisal). The two most commonly used methods are the single and double tear test whereby in the single tear test the force is applied in one direction whereas in the double tear test, the force is applied in two opposite directions (Nalbat *et al.*, 2016). For this study, the double tear test was conducted. There was a significant difference between the tearing strength of *C. arabica* pulp leather and mimosa leather although the tearing strength of both leathers surpassed the minimum recommended values of 20N/mm2. The tearing strength for both coffee and mimosa were higher in the direction of fibers perpendicular to the backbone as compared to the direction parallel to the backbone. A study by Nalyanya *et al.*, (2018) in Kenya, agreed with the findings of this study as the tearing strength for the leather taken after the tanning stage was 88.20 and 74.60 perpendicular and parallel to the backbone respectively.

5.4.4. Ball Burst

The grain crack and grain burst are important properties for shoe upper leather especially for the lasting operation in shoe making. The leather is elongated in all directions until it bursts with the height at appearance of the first crack taken as the grain crack and the height where the leather bursts taken as the grain burst. The minimum recommended values for both the grain crack and ball burst are 6.5mm and 7.0 mm respectively.

There was a significant difference between the grain crack and grain burst of *C. arabica* pulp leather and mimosa tanned leather with the coffee leather not meeting the minimum required standards for this test whereas mimosa tanned leather met the set standards. Dennis *et al.*, (2020) in his study of *Plectranthus barbatus* in Kenya found the grain crack and grain burst of the mimosa tanned goatskin to be 7.7 mm and 8.2mm respectively. A study by Oliveira *et*

al., (2007) in Brazil found the ball burst for tanned goatskins to be 10.34mm though differing depending on breed.

5.4.5. Flex Endurance

Flex endurance is a test commonly applied to leathers meant for the shoe industry although also done for leathers used to make products that encounter flex action in their use. This test shows the resistance of the leather finish to form cracks and creases when subjected to the flex action (Nalyanya *et al.,* 2018). The *C. arabica* tanned leather failed the test at 10000 flexes for both the samples perpendicular and parallel to the backbone with the failure observed as creases and a change in colour from blackish brown to brown. This can be attributed to the case hardening of the leather during tannage as there wasn't complete and proper penetration into the pelt and as a result leading to the stacking together of the fibers and resulting into reduced flexibility of the leather (Covington, 2009).

5.5.Conclusion

The study on *C. arabica* pulp as a source of tannins had the following conclusion:

1. Coffee arabica pulp from Yadini farm was found to have condensed tannins with the tannin content of 5.04 %.
2. The tanning strength of coffee pulp was established as 2.26 which exceeded the minimal recommended value of 1.5 though was lower compared to mimosa at 2.82.
3. The shrinkage temperature of coffee arabica pulp leather at 62 ^{o}C was high enough for the pelt to be considered tanned but very low in comparison to mimosa tanned leather at 83^{o}C.
4. The tensile strength and tear strength of the coffee pulp leather exceeded the minimum recommended values of 12 and 20 respectively though were still lower in comparison to mimosa tanned leather.

5. Coffee pulp tanned leather failed to meet the minimum recommended values for ball burst and flex endurance tests whereas mimosa tanned leather met and exceeded the recommended values of 7.0 for ball burst and 100000 flexes for flex endurance.
6. The tannin content, tanning strength, tensile strength, shrinkage temperature, ball burst, flex endurance and tear strength for coffee pulp were significantly difference $p<0.05$ from the values of mimosa.

5.6.Recommendations

The findings on the study of *C. arabica* lead to the recommendations that:

1. More research should be carried out on the reason why penetration of *C. arabica* pulp tannins was not fully successful in order to fully investigate the action of the *C. arabica* pulp tannins to collagen.
2. Further research to be done on the molecular size and astringency of tannins obtained from *C. arabica* pulp.
3. Further research should be carried out on the possibility of using *C. arabica* pulp tannins as retanning agents and their effect when used in combined tannage with syntans, other vegetable tannins and mineral tanning agents.

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APPENDICES

Appendix 1: Process recipe for hide powder

Operations	Products	Percentage	Run time	Remarks
Soaking	Water @ room temperature. Soaking enzymes Sodium carbonate Detergents	200% 1% 0.3% 1%		Stir for 1 hours and leave overnight (18hrs)
liming	Water @ room temperature Sodium sulphide lime	200% 3% 2%	Stir for 30 minutes and leave overnight	Check pH 12.
Deliming	Ammonium sulphate Oxalic acid	2.5% 0.5%	Stir for 30 minutes and leave overnight	pH around 8.0-8.2
Bating	Warm water Bating enzymes	100% 0.5%		
Pickling	Water at room temperature Salt Formic acids Sulphuric acids	100% 8% 0.5% 0.5%	Run for 20 min and leave overnight	Check Baume (Be 8)
Drain and wash with clean water				
The pickled pelt was put in acetone and later dried under a shade				
Grading the hide in to powder using a star mill				

Appendix 2: Recipe for the tanning of the leather.

operations	products	percentage	Run time	Remarks
Soaking	Water @ room temperature Soaking enzymes Sodium carbonate detergents bacteriocide	200% 1% 0.3% 1% 0.5%	Stir for 1 hours and leave overnight (18hrs)	
liming	Water @ room temperature Sodium sulphide lime	200% 3% 2%	Stir for 30 minutes and leave overnight	Check pH (12.00)
Deliming	Ammonium sulphate Sodium bicarbonate	2.5% 0.5%	Run for 40 min and leave overnight	pH around 8.0-8.2
Bating	Warm water microbate	100% 0.5%		
Pickling	Water at room temperature Salt Formic acids Sulphuric acids	100% 6% 0.5% 0.5%	Run for 20 min and leave overnight	Check Baume (Be 8)

Tanning procedure

process	products	percentage	Run time	comments
Neutralization	water at room temperature Sodium bicarbonate	100% 2.5	1 hour	 pH 6.5
Tanning	Vegetable tannin Vegetable tannin Vegetable tannin Formic acid	 5 5 5 1	Run for 6hours and leave overnight for each addition	 pH 3.8-4.2
Neutralization	Water at room temperature Sodium bicarbonate	100% 1.5	Run for 2 hours	
Fatliquoring	Vegetable fatliquor Formic acid	4 1	Run for 2 hours Run for 1 hour	pH- 3.5

Appendix 3: Physical characteristics of leather observed.

Moisture t test

Two-sample t-test

Variate: moisture

Group factor: sample

Test for equality of sample variances

Test statistic F = 14.77 on 11 and 6 d.f.

Probability (under null hypothesis of equal variances) = 0.00

Note: strong evidence of unequal sample variances -
variances estimated separately for each group.

Summary

Sample	Size	Mean	Variance	deviation	of mean
coffee	12	10.313	0.5836	0.7639	0.2205
mimosa	7	8.057	0.0395	0.1988	0.0751

Difference of means: 2.256
Standard error of difference: 0.233

95% confidence interval for difference in means: (1.754, 2.758)

Test of null hypothesis that mean of moisture with sample = coffee is equal to mean with sample = mimosa

Test statistic t = 9.68 on approximately 13.37 d.f.

Probability < 0.001

Solids t test

Two-sample t-test

Variate: solids
Group factor: sample

Test for equality of sample variances

Test statistic F = 14.89 on 11 and 6 d.f.

Probability (under null hypothesis of equal variances) = 0.00

Note: strong evidence of unequal sample variances -
variances estimated separately for each group.

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
coffee	12	89.68	0.5885	0.7672	0.2215
mimosa	7	91.94	0.0395	0.1988	0.0751

Difference of means: -2.261
Standard error of difference: 0.234

95% confidence interval for difference in means: (-2.765, -1.757)

Test of null hypothesis that mean of solids with sample = coffee is equal to mean with sample = mimosa

Test statistic t = -9.67 on approximately 13.35 d.f.

Probability < 0.001

Solubles t test

Two-sample t-test

Variate: solubles
Group factor: sample

Test for equality of sample variances

Test statistic F = 5.24 on 11 and 6 d.f.

Probability (under null hypothesis of equal variances) = 0.05

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
coffee	12	7.28	0.15465	0.3932	0.11352
mimosa	7	86.04	0.02952	0.1718	0.06494

Difference of means:	-78.768
Standard error of difference:	0.158

95% confidence interval for difference in means: (-79.10, -78.43)

Test of null hypothesis that mean of solubles with sample = coffee is equal to mean with sample = mimosa

Test statistic t = -498.27 on 17 d.f.

Probability < 0.001

Non tans t test

Two-sample t-test

Variate: non_tans
Group factor: sample

Test for equality of sample variances

Test statistic F = 3.81 on 6 and 11 d.f.

Probability (under null hypothesis of equal variances) = 0.05

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
coffee	12	2.24	0.0629	0.2507	0.0724
mimosa	7	22.54	0.2395	0.4894	0.1850

Difference of means:	-20.300
Standard error of difference:	0.168

95% confidence interval for difference in means: (-20.65, -19.94)

Test of null hypothesis that mean of non_tans with sample = coffee is equal to mean with sample = mimosa

Test statistic t = -120.62 on 17 d.f.

Probability < 0.001

Tannins t test

Two-sample t-test

Variate: tans
Group factor: sample

Test for equality of sample variances

Test statistic F = 11.72 on 6 and 11 d.f.

Probability (under null hypothesis of equal variances) < 0.001

Note: strong evidence of unequal sample variances -
variances estimated separately for each group.

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
coffee	12	5.03	0.0294	0.1715	0.0495
mimosa	7	63.51	0.3448	0.5872	0.2219

Difference of means:	-58.483
Standard error of difference:	0.227

95% confidence interval for difference in means: (-59.03, -57.94)

Test of null hypothesis that mean of tans with sample = coffee is equal to mean with sample = mimosa

Test statistic t = -257.20 on approximately 6.60 d.f.

Probability < 0.001

Tanning strength t test

Two-sample t-test

Variate: strength
Group factor: sample

Test for equality of sample variances

Test statistic F = 5.37 on 11 and 6 d.f.

Probability (under null hypothesis of equal variances) = 0.05

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
coffee	12	2.261	0.03857	0.1964	0.05670
mimosa	7	2.819	0.00718	0.0847	0.03203

Difference of means: -0.5577
Standard error of difference: 0.0789

95% confidence interval for difference in means: (-0.7241, -0.3914)

Test of null hypothesis that mean of strength with sample = coffee is equal to mean with sample = mimosa

Test statistic t = -7.07 on 17 d.f.

Probability < 0.001

Tensile strength for parallel t test

Two-sample t-test

Variate: Tens_Para
Group factor: Sample

Test for equality of sample variances

Test statistic F = 1.22 on 15 and 15 d.f.

Probability (under null hypothesis of equal variances) = 0.71

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
coffee pulp	16	14.72	4.157	2.039	0.5097
mimosa	16	24.19	5.064	2.250	0.5626

Difference of means: -9.471
Standard error of difference: 0.759

95% confidence interval for difference in means: (-11.02, -7.921)

Test of null hypothesis that mean of Tens_Para with Sample = coffee pulp is equal to mean with Sample = mimosa

Test statistic t = -12.48 on 30 d.f.

Probability < 0.001

Two-sample t-test

Variate: Tens_per
Group factor: Sample

Test for equality of sample variances

Test statistic F = 4.14 on 15 and 15 d.f.

Probability (under null hypothesis of equal variances) = 0.01

Note: strong evidence of unequal sample variances -
variances estimated separately for each group.

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
coffee pulp	16	19.09	2.563	1.601	0.4003
mimosa	16	27.20	10.608	3.257	0.8143

Difference of means: -8.108
Standard error of difference: 0.907

95% confidence interval for difference in means: (-9.990, -6.225)

Test of null hypothesis that mean of Tens_per with Sample = coffee pulp is equal to mean with Sample = mimosa

Test statistic t = -8.94 on approximately 21.85 d.f.

Probability < 0.001

Tear strength for parallel to backbone.

Two-sample t-test

Variate: tear_para
Group factor: Sample

Test for equality of sample variances

Test statistic F = 2.66 on 15 and 15 d.f.

Probability (under null hypothesis of equal variances) = 0.07

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
coffee pulp	16	48.00	200.2	14.15	3.538
mimosa	16	75.97	75.4	8.68	2.171

Difference of means:	-27.971
Standard error of difference:	4.151

95% confidence interval for difference in means: (-36.45, -19.49)

Test of null hypothesis that mean of tear_para with Sample = coffee pulp is equal to mean with Sample = mimosa

Test statistic t = -6.74 on 30 d.f.

Probability < 0.001

Tear strength for perpendicular to backbone t test.

Two-sample t-test

Variate: tear_perpe
Group factor: Sample

Test for equality of sample variances

Test statistic F = 6.87 on 15 and 15 d.f.
Probability (under null hypothesis of equal variances) < 0.001

Note: strong evidence of unequal sample variances -
variances estimated separately for each group.

Summary

Sample	Size	Mean	Variance	deviation	of mean
coffee pulp	16	38.12	9.77	3.126	0.782
mimosa	16	72.08	67.13	8.193	2.048

Difference of means: -33.959
Standard error of difference: 2.192
95% confidence interval for difference in means: (-38.54, -29.38)

Test of null hypothesis that mean of tear_perpe with Sample = coffee pulp is equal to mean with Sample = mimosa

Test statistic t = -15.49 on approximately 19.28 d.f.

Probability < 0.001

Two-sample t-test

Variate: el_para
Group factor: Sample

Test for equality of sample variances

Test statistic F = 1.13 on 15 and 15 d.f.

Probability (under null hypothesis of equal variances) = 0.81

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
coffee pulp	16	14.44	4.939	2.222	0.5556
mimosa	16	45.74	5.605	2.368	0.5919

Difference of means:	-31.307
Standard error of difference:	0.812

95% confidence interval for difference in means: (-32.97, -29.65)

Test of null hypothesis that mean of el_para with Sample = coffee pulp is equal to mean with Sample = mimosa

Test statistic t = -38.57 on 30 d.f.

Probability < 0.001

Two-sample t-test

Variate: el_per
Group factor: Sample

Test for equality of sample variances

Test statistic F = 1.41 on 15 and 15 d.f.

Probability (under null hypothesis of equal variances) = 0.51

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
coffee pulp	16	9.89	1.397	1.182	0.2954
mimosa	16	41.92	1.968	1.403	0.3507

Difference of means:	-32.032
Standard error of difference:	0.459

95% confidence interval for difference in means: (-32.97, -31.10)

Test of null hypothesis that mean of el_per with Sample = coffee pulp is equal to mean with Sample = mimosa

Test statistic t = -69.85 on 30 d.f.

Probability < 0.001

Grain crack t test

Two-sample t-test

Variate: G_C
Group factor: Sample

Test for equality of sample variances

Test statistic F = 3.52 on 15 and 15 d.f.

Probability (under null hypothesis of equal variances) = 0.02

Note: evidence of unequal sample variances -
variances estimated separately for each group.

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
coffee pulp	16	4.521	0.3113	0.5579	0.1395
mimosa	16	7.468	0.0884	0.2973	0.0743

Difference of means: -2.948
Standard error of difference: 0.158

95% confidence interval for difference in means: (-3.275, -2.620)

Test of null hypothesis that mean of G_C with Sample = coffee pulp is equal to mean with Sample = mimosa

Test statistic t = -18.65 on approximately 22.88 d.f.

Probability < 0.001

Grain burst t test

Two-sample t-test

Variate: G_B
Group factor: Sample

Test for equality of sample variances

Test statistic F = 3.62 on 15 and 15 d.f.

Probability (under null hypothesis of equal variances) = 0.02

Note: evidence of unequal sample variances -
variances estimated separately for each group.

Summary

Sample	Size	Mean	Variance	Standard deviation	Standard error of mean
coffee pulp	16	5.934	0.07855	0.2803	0.07006
mimosa	16	8.252	0.02170	0.1473	0.03683

Difference of means: -2.3187
Standard error of difference: 0.0792

95% confidence interval for difference in means: (-2.483, -2.155)

Test of null hypothesis that mean of G_B with Sample = coffee pulp is equal to mean with Sample = mimosa

Test statistic t = -29.29 on approximately 22.70 d.f.

Probability < 0.001