EVALUATION OF TANNING STRENGTH AND QUALITY OF LEATHERS PRODUCED BY SELECTED VEGETABLE TANNING MATERIALS FROM LAIKIPIA COUNTY, KENYA

Alex Nduru Kuria, BSc (Animal Health, Production and Processing, JKUAT)

A thesis submitted in partial fulfillment for the requirements of the Degree of Master of Science in Leather Science of the University of Nairobi

Department of Public Health Pharmacology and Toxicology

Faculty of Veterinary Medicine

University of Nairobi

November 2015

DECLARATION

This thesis is my original work and has not been presented for a degree award in any other university.

Signature …….. Date…….

Alex Nduru Kuria

This thesis has been submitted for examination with our approval as University supervisors.

Prof. Jackson. N. Ombui, BVM, MSc, PhD (University of Nairobi)

Signature …….. Date…….

Dr. Arthur Onyuka, BSc, PhD (Kenya Industrial Research and Development Institute).

Leather Division

Signature…… Date ……

DEDICATION

This thesis is dedicated to my father Peter Kuria, mother Joyce Nyambura, my sister and my brothers for their prayers and continued support.

ACKNOWLEDGEMENT

I thank the almighty God for blessing me with good health and knowledge and for his provision which has enabled me to go through this programme. I would like to thank the Department of Public Health, Pharmacology and Toxicology of the University of Nairobi for according me a study opportunity. I also wish to express my appreciation to my supervisors Prof. Jackson. N. Ombui and Dr. Arthur Onyuka for their guidance, advice, and encouragement while preparing my research proposal, carrying out the field work and when writing up the thesis.

I also appreciate Mr. Joseph Mbogo and Mr. Joel Mwondu from the Department of Public Health, Pharmacology and Toxicology for their valuable advice and encouragement.

I would also like to thank Kenya Industrial Research and Development Institute (KIRDI) for allowing me to use their facilities. I would also like to thank Mr. Alvin Sasia of KIRDI for his technical assistance in the laboratory. It would have been a lonely laboratory without him.

I would like to express my deepest gratitude to tanners from Laikipia County who provided information on the types of the tree species they use and their method of tanning hides and skins.

Special thanks are also extended to Miss Kaimenyi and Mr. Kamau for their prayers and moral support that enabled me to complete this work. May the almighty God bless you all.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

BIS: Bureau of Indian standards

CD: Circular dichroism

HPLC: High pressure liquid chromatography

IULTCS: International union of leather technologist and chemist society

IUP: International union for physical testing

MS: Mass spectrophotometer

NT: Non- tannins

TS: Total solubility

UNIDO: United Nations industrial development organization

UV: Ultra-violent

DEFINITION OF TERMS

Bating: Is a processing step that follows liming. Enzymes are used to impart softness, stretch and flexibility to the final leather.

Beamhouse: Is a section of a tannery where fleshing, liming, unhairing and bating and pickling processes are done.

Deliming: Is the process which removes the lime from the hides coming from the beamhouse

Flaying: Process of removal of the hide or skin from the animal carcass.

Fleshing: Process of removing any adipose tissue on the flesh side of the skins and usually done after liming.

Grain: Indicates the outer hair side of a hide or skin after the hair and epidermis have been removed

Grain crack: A physical test that indicate a point at which the grain surface of the leather cracks after distention.

Grain burst: A physical test that indicate a point at which the grain surface of the leather burst after distention

Insoluble: The amount of materials present in any vegetable tanning materials that are not soluble in water.

Leather tanning: Numerous steps involved in converting animal hide and skins into finished leathers.

Non-tannins: Consists of sugary substances, gums, soluble mineral salts and acids that are extracted together with the tannins.

Pelt: Hide or skin that is being processed in the beamhouse.

Tannins: Are water soluble polyphenolic compounds having a molecular weight of 500-20000 Da and have ability to precipitate proteins and alkaloids.

Tannin content: The proportion of tannins in the vegetable tanning materials.

Tanning materials: Any materials that are used in leather production and they include woods, barks, fruits and leaves from various plants.

Tanning strength: Ratio of tannins to soluble non-tannins and indicate the ability of the tanning liquor to produce good leathers.

Tanning waste materials: Parts of plants e.g. barks, wood, fruits and leaves that are disposed to the environments after extraction of tannins.

Total solids: The amount of solid materials contained in any tanning materials. This is generally obtained by deducting the moisture content from the total weight of the materials.

Total soluble: The total amount of water soluble materials present in any vegetable tanning materials.

Residual tannin levels: Amount of tannins that remain in the waste materials after extraction of the tanning liquors.

ABSTRACT

Tanning is a processing mechanism which prevents the collagen fibrous protein in animal skins from putrefaction which lead to production of hydrothermal stable product commonly known as leather. Tannins from plants are some of the agents that are used in leather production in a process called vegetable tanning. Vegetable tanning is an ecofriendly method of tanning compared to environmental polluting chromium based method of tanning that is commonly used in commercial tanning. However vegetable tanning have not been widely used in commercial tanning because mimosa, the only available commercial vegetable tanning materials is expensive compared to chromium.

A study was conducted to determine the tanning potential of three locally available plants in Laikipia county namely: *Acacia nilotica, Acacia xanthophloea and Hagenia abyssinica* . The study determined the tannin content and tanning strength of the above named three plant species and their suitability for tanning hides and skins. The hide powder method was used in determining the amounts of tannins while the quality of leathers was determined by evaluating their physical properties using standard IUP methods. The leathers were produced using vegetable tanning materials from the three study plants and commercial mimosa was used as a control. The student t-test was used to compare the mean values of the tannin content and the physical properties of produced leathers.

The study found *Acacia nilotica, Acacia xanthophloea and Hagenia abyssinica* to contain 16.8%, 23.8%, 11.73% tannins respectively. *Acacia nilotica* had a tanning strength of 1.5 while *Acacia xanthophloea* and *Hagenia abyssinica* had a tanning strength of 3.3 and 2.1 respectively.

There was a significant difference in the mean tannin levels between the three vegetable tanning materials identified when compared with commercial mimosa ($p= 0.001$).

The leathers tanned with *Acacia nilotica* had a tearing strength of 42.67 N, tensile strength of 28.62 N/mm^2, grain crack of 7.66 mm, grain burst of 8.42 mm, endured 100,000 flexes, and shrunk at temperature of 82.5^{0}C. The leathers tanned with *Acacia xanthophloea* had a tearing strength of 34.92 N, tensile strength of 20.36 N/mm^2, grain crack of 7.98 mm, grain burst of 8.81 mm, endured 100,000 flexes and shrunk at temperature of 85^{0}C. The leathers tanned with *Hagenia abyssinica* had a tearing strength of 31.25 N, tensile strength of 27.91 N/mm^2, grain crack of 8.97 mm, grain burst of 9.35 mm, endured 100,000 flexes, and shrunk at temperature of 80^{0}C. The leathers tanned with commercial mimosa had a tearing strength of 34.22 N, tensile strength of 28.81 N/mm^2, grain crack of 8.21 mm, grain burst of 8.76 mm, endured 100,000 flexes, and shrunk at temperature of 83^{0}C.

A comparison of physical properties of leathers tanned with materials from *Acacia nilotica*, *Acacia xanthophloea* and *Hagenia abyssinica* and those tanned with commercial mimosa indicated no significant difference in tensile strength, flexing endurance and tearing strength $p > 0.05$. In addition, there was no significant difference between leathers tanned with mimosa and *Acacia xanthophloea* for grain crack ($p= 0.67$) and grain burst ($p= 0.77$) tests. Leather tanned with *Acacia nilotica* had a significant difference in grain crack ($p = 0.01$) but no significant difference ($p = 0.36$) in grain burst when compared with mimosa. The results also indicated a significant difference on grain crack ($p= 0.03$) and grain burst ($p= 0.02$) in *Hagenia abyssinica* and mimosa vegetable tanned leathers.

In conclusion this study found all the vegetable tanning materials tested to have more than 10% tannins and a tanning strength of more than 1.5 required for commercial extraction. The quality of leathers tanned with these vegetable tanning materials was comparable to those tanned with commercial mimosa and all of them had more than the minimum set standards. It was recommended that the selected vegetable tanning materials from Laikipia County be exploited commercially for leather production.

CHAPTER ONE: INTRODUCTION

1.1 Background information

Processing of hides and skins into leather is one of the key agro-processing industries in Kenya with a high potential towards commodity development that addresses pertinent issues of socio-economic importance and positively impacts on rural development, creation of wealth and employment (Mwinyihija, 2010). Currently the country has 15 tanneries and most of these tanneries are processing 88% of raw hides and skins up to wet blue and 2% finished leather. The remaining 10% is exported in raw form. Most of the tanneries are located in Nairobi, Machakos and Kiambu Counties, far from the livestock rearing regions. A large part of the Kenyan landscape (80%) falls under arid and semi-arid zones, which contribute 70% of the total livestock population (Mwinyihija, 2010). Leather industry depends largely on locally available large livestock resource base in these areas where hides and skins are the by- products. The hides and skins in Kenya come from cattle, camel, sheep and goat and also from non-conventional livestock such as ostrich, crocodiles and fish. Leather industry contributes an estimated 4% to agricultural gross domestic products. In the recent past the country produced an average of 6 million skins from sheep and goat, 2.4 million cattle hides and 20,000 camel hides (Markcurtis, 2010). In Laikipia County the current annual production for hides and skins stands at 1,867 and 19,000 respectively all valued at ksh 29 million (Weru, 2014).

Most of the pastoral communities in arid and semi-arid parts of Kenya have been making leather goods such as bags, wallets, leather straps and garments. Tanning which is the processing of raw skins and hides into leather seems to have been left in the hands of only the local tanners in Laikipia county who use simple and outdated technologies. Also few people learn tanning

technique and most of the practitioners are old which means when the old people die they die with their trade. As Professor H.R. Procter, one of pioneers in applying scientific principles to leather manufacture, said, “Science must follow before it can lead” (Reed, 2013) ; there is a need to study the process the local tanners use and analyze the tanning strength of the vegetable tanning material they use. Soluble components present in the bark, leaves or fruit of very many different species of plants have been found to have tanning properties (Bickley, 1999). The tanner must choose the most appropriate tannin or mixture of tannins to produce the desired properties in the leather. The process of extracting these compounds also yields a complex mixture of other materials (the "non-tannins") which, while having no tanning power in their own right, contribute significantly in determining the properties of the resultant leather (Reed, 2013). The composition of the extract varies markedly between different plant species and is affected by various conditions during extraction in particular, the temperature and pH (Bickley, 1999).

The vegetation in Laikipia County is characterized of semi-arid African savanna predominantly grassy savanna bush land, with patches of woodland and open grassland. Dominant trees include species in the general Acacia, Euphorbia, Balanites, and Boscia (Larkin, 2013). There are different species of acacia trees that are used in the tanning of hides and skins in this area. Some of the species include: *Acacia drepanolobia, Acacia seyal, Acacia totolis, Acacia nilotica, Acacia xanthophloea, Acacia mearsii* and *Acacia raddiana* (Rohner and ward, 1997). The tannin content in these species varies with the bark thickness, age of the trees and average annual rainfall and differs from base of the truck upward, the branch having low tannin content (Donlop, 2005). Tests carried out in Kenya have shown that the tannin content of *Acacia nilotica* bark and

bark extracts is low (11.5-13%) compared to *Acacia mearnsii* (49.5-55%) (Faggs and Mugedo, 2005). *Acacia drepanolobia* is the dominant tree species in Laikipia County comprising approximately 95% of the woody type, while *Acacia xanthophloea* which has been a common feature along the edge of rivers and in wetlands are now on decline owing to the destruction by the elephants and burning of the marshland (Young *et al*., 1998).

In Kenya today, leather industry is continuing to improve its methods and processes of leather manufacture with emphasis on environmental protection. Harvesting of vegetable tannins can lead to deforestation if not controlled. This is because most rural tanners do not know the tanning strength of the vegetable tanning materials they use and therefore, they end up using an excess amount to guarantee the tanning process. The finding of this study will help the rural tanner to know the plants with high tannin content and the correct amount of vegetable tanning material to use and therefore prevent indiscriminate cutting of Acacia trees, reduce wastage and improve quality of the end product.

1.2 Statement of the problem and justification of the study

Leather industries in developing countries are ranked among the most polluting industries. These industries generate waste contaminated with high toxic levels of chromium. Chromium is used in the tanning process, but about 40% of the amount used remains in the waste that is disposed to the environment. These industries are facing a lot of solid waste treatment and disposal problems and many tanneries have been closed for not meeting the required level of chromium, bio-chemical oxygen demand and total dissolved solid in their effluents. These industries also generate huge amounts of chromium contaminated solid and liquid waste which emit obnoxious

smell to the environment. Vegetable tannins have been identified as an alternative to chrome tanning but they have not been widely used because they are not readily available and are expensive. The only vegetable tanning materials available commercially is mimosa from *Acacia mearnsii* which is expensive to many tanners. However a number of cottage tanners continue to use various plants as tanning materials. There is renewed research effort to validate some of the materials being used by cottage tanners and also to discover new plants species with high tannin content for commercial exploitation. The aim of this study was to validate the vegetable tanning materials used by cottage tanners in Laikipia County with a view of determining their tanning strength and potential for commercial exploitation. The findings of this study will lead to optimization of vegetable tanning using locally available materials which will reduce the cost of leather production and environmental pollution associated with chrome tanning.

1.3 Objectives

1.3.1 General objective

To evaluate the tanning strength of vegetable tanning materials found in Laikipia County and their suitability for tanning hides and skins.

1.3.2 Specific objectives

- To identify the types and sources of vegetable tanning materials found in Laikipia County.
- To evaluate the tanning strength of vegetable tanning materials.
- To compare the physical properties of standard mimosa and Laikipia vegetable tanned leathers.

CHAPTER TWO: LITERATURE REVIEW

2.1 History of Leather Tanning

The term tannin was used the first time by Seguin in 1796 to indicate a substance present in vegetable extracts capable of forming insoluble complexes with collagen by preventing the action of proteolytic enzymes that could affect the physical condition of the skin (Eldin *et al*., 2014). Tanning of animal skin dates back to prehistoric time (Seigler, 2005). The ancient Egyptians made such durable leather that specimens over 3,000 years old have been discovered in almost perfect condition. It went on to give evidence of oil tanning which has been found in leather from Egyptian tombs (Seigler, 2005). The early Greeks and Romans also made contributions to the science of leather making. Some of their methods are still in use today. Leather is made from hides and skins as the raw materials. The term hide refers to outer covering of mature animals of the larger type such as cattle and buffalo. The outer covering derived from mature animals of the smaller type such as sheep, goats and pigs as well as reptiles, fish and young ones of the larger group such as calf is usually referred to as skin (Mwinyihija, 2010).

2.2 Pre-tanning of hides and skins

Hides and skins contain some components that are mostly removed before vegetable tanning. Some of the components that are mostly eliminated include keratins, elastin, reticulin, glyco-proteins, albumins, and globulins. In leather manufacture the protein collagen remains for conversion into the leather because it is fibrous (Reed, 2013, Sah, 2013). The processes involved in removing these unwanted components in hides and skins before vegetable tanning include curing, soaking, fleshing, unhairing/ liming, deliming and bating (Sah, 2013).

Curing is a process that prevents the decomposition of hides and skins after flaying before they are taken to the beamhouse for processing. The hides and skins may be wet salted, dry salted sundried or shade dried.

Soaking is the first operation in the tannery, where the fresh or preserved hides and skins are treated with water for making them clean and soft (Marion and Rey, 2006). The main purpose of soaking is to remove salt used during curing, rehydrate the dry hides and skins and to get rid of unwanted materials such as dung, blood and soil. The duration of soaking depends on the condition of preserved hides and skins (Yopici *et al*., 2008).

The second step in leather processing is the removal of hairs and other components from the skins which are not supposed to be transferred into the leather. During this process the hair is removed by putting the hides or skins in a chemical or depilating agent, which destroy the hair by attacking the hair root so that it can easily be, removed (Flaherty *et al.*, 1978). It also loosens the epidermis and removes soluble skins proteins such as albumins, globulins and glycoproteins. In most tanneries, lime and Sodium sulphide are normally used (Souza and Gutters, 2012). The hair is loosed and disintegrated due to high pH of lime liquor. Prolonged treatment causes weakening of the whole of the hair but this is more rapidly brought about by accelerators such as sodium sulphide added to the liquors (Habib *et al*., 2015). The weakening of the hair is dependent on the breakdown of the disulphide link of the amino acid, cysteine which is a characteristic of keratins (Yopici *et al*., 2008). The higher pH also cause swelling and splitting of the fibre bundles (Sarkar, 1995). The general loosening of the fibre weave is influenced by the amount of the osmotic swelling which allows both loosening of the fibre structure and lateral

splitting of the fibres into smaller units (Ramasami and Prasad, 1991). The splitting of the fibre bundles allows the tannins to penetrate easily during tanning. Fleshing is also done after liming to remove excess flesh, fat and muscle and this allows the deliming chemicals and enzymes to penetrate easily into the pelt.

Deliming is the process of adjusting the pH in between 8-9 in order to enhance enzymatic activity which converts some of the proteins into soluble forms. The pH correction from 12-12.5 to 8-9 is done using ammonium chloride in case of soft leathers and ammonium sulphate in case of hard leathers (SLTC, 1999). Deliming reduces the swelling/ plumping of the pelt.

Bating is an enzymatic process performed to impart softness, stretch and flexibility to the leather. During bating, scuds are loosened and other unwanted proteins are removed and this increases the degree of stretch. Bating de-swells swollen pelts and prepares pelt for tanning. It makes the grain surface of the finished leather clean, smooth and fine (Santos and Gutters, 2006). It is performed at a temperature of around 37^{o}C which is the optimum temperature for enzymatic actions.

2.3 Tanning of hides and skins

The global leather industries have been in existence for over 400 years and during that time technologists have been concerned to impose stability to the raw hides and skins (Covington, 2009). Until the advent of chromium tanning, toward the end of 19th century, the options available to the tanner were limited to the following processes: vegetable tanning, aluminium tawing, oil tanning and brain and smoke tanning (Covington, 2009).

Many fat and oils have tanning properties (Lawal and Odums, 2015). The primitive man noticed that the skins in which they wrapped themselves retained their natural softness and lasted longer when their body happened to be smeared with fats than at other times, eventually they concluded that applying fats and oils into the skins would achieve the same results (Sarkar, 1995). Oil tanning produces leather with characteristics quite different from other leathers (Lawal and Odums, 2015). The leather readily absorbs water, but on wringing the leather releases moisture again just easily. Oil tanned leathers readily absorb grease and hence they are mainly used for washing cars and glass windows. The disadvantage with this type of leather is that it has a lower shrinkage temperature of 60^0C.

Leather can also be made using brain and smokes. The oil in an animal brain provide a natural tanning agent and each animal has a brain just enough to tan its entire hides. The final steps in brain tanning is smoking the brain tanned leathers. The leather is more durable if they are smoked for several hours in a smokehouse (Boren *et al*., 2009).

The manufacture of aluminium leathers is called tawing. The production of alum leather became very widespread during the middle age and was used for production of book binding leathers, gloving leathers, ladies shoes leathers and fur skins (Covington, 2011, Lawal and Odums, 2015). Evidence is also there to show that as early as 800 B.C, people discovered the mineral salt, alum, and began using it as a tanning agent. The Assyrians, Babylonians, Greeks, and Sumerians used this mineral method of tanning because it was much faster than previous techniques (The World book Encyclopedia, 2001). Aluminium in the alum combine with the leather fibres and this can be observed by the increased shrinkage temperature of the leather (Haroun *et al*., 2009). The

leather is sensitive to being washed in water unlike normal leathers that can withstand washing. When alum leathers are thoroughly immersed in water the tanning salts are washed out and sulphuric acid is produced. When dried the resulting leather is hard and inflexible having the characteristics similar to those of dried raw pelt (Vest, 1999).

Today the most important tanning method is chrome tanning which accounts for approximately 85% of the world's leather production (Tegtmeyer and Kleban, 2013). The advantages of chrome tanning materials over the other commercially available tanning materials are the high speeds of protein fixation, an extra ordinary dyeing suitability, low chemical costs and excellent hide preservation. Unfortunately, only a fraction of chromium salts used in the tanning process (60%) reacts with the hides and the skins. The rest of the salt (40%) remains in the tanning exhaust bath and are subsequently sent to effluent treatment plant where the chromium salts end up in the sludge (Mwinyihija *et al*., 2006). One of the major emerging environmental problems in tanning industry is the disposal of chromium contaminated sludge produced as by-products of the waste water treatment (Moorthy and Mekonnen, 2013). Tannery effluent containing chrome severely affects the mitotic processes and reduces seed germination in extensively cultivated pulse crops (Mole, 1993). At high concentrations chromium is toxic, mutagenic and teratogenic (Bielicila *et al.,* 2005). Due to the above mentioned disadvantages of chrome tanning the tanners are now encouraged to adapt new ecofriendly methods of tanning such as vegetable tanning materials (Moorthy and Mekonnen, 2013).

2.4 Vegetable tanning

Vegetable tanning involves use of tannins derived from plants. Vegetable tannins are water soluble polyphenolic compounds having molecular weights of 500 to 20,000 Da (Khanbabaee and Van, 2001) and besides giving the usual phenolic reactions, they have special properties such as the ability to precipitate alkaloids and proteins (Haslam, 1989). The process, termed as vegetable tanning, is one of the oldest known leather making processes and was done by treating the hides and skins with leaves and barks containing tannin (vegetable tannins). Many ancient peoples tanned their leather by placing layers of bark, leaves, and fruit over the hides and adding water. This process took months, and in the case of thick skins, even years according to the World book Encyclopedia (2001). Due to increasingly strict requirements for leather and with regard to recycling of leather wastes, the manufacture of chromium-free leather has become very important (Plavan, 2009). Vegetable tanning is the most eco-friendly method of tanning compared to other methods and it discharge minimum pollutants to the environment (Jianzhong *et al*., 2009). Some time ago, the use of vegetable tannins was almost exclusively related to sole leather production (Reed, 2013). Today it is possible to obtain high quality environmentally friendly products: leathers with good softness, sponginess, tightness and embossing retention properties that can be refined in many ways in order to adapt to different uses. It is also possible to obtain high yield heavy leathers, which are compact, firm and flexible (Ogiwara, 1980). Vegetable tanned leather has excellent fullness, moldering properties, wear resistance and air permeability; hence it is of great significance in the reduction of chrome pollution in leather making process (Faxing *et al.,* 2005). Vegetable tanned leather is used in making heavy leather such as furniture leather and also light leathers such as shoe upper leather. Worldwide, researchers are paying particular attention to the use of vegetable tanning agents to replace

chrome tanning agents and progress has already been achieved. The result is a superior product in every aspect, combining excellent technical characteristics, vintage-looking materials, warm colors and unique aspects that last and improve over their lifetime (Kaloka and Moreki, 2011). Vegetable tannins are also used in the retanage process to achieve a variety of purpose and are applicable to different kinds of chrome leathers. The objective of the process is to fill the looser and softer parts of the leather in order to produce leather of more uniform physical properties to allow the production of unlimited footwear and to allow rapid finishing and delivery to customers.

Tannins are distributed in many species throughout the plant kingdom. They are found in both dicotyledonous and monocotyledonous plants (Ogiwara, 1980). They are found in approximately 80% woody and 15% herbaceous dicotyledonous species and can occurs at high levels in some forage, feed and food (Bryant *et al*., 1992). A study conducted by Mole on the distribution of tannins in both dicot and monocot, showed that 73% of the species from Fagaceae family contains tannins while those of acaceas, Mimosaceae, only 39% of the species tested contain tannins (Mole,1993). The best families of which all families tested contain tannins are: Aceracea, Combretaceae, Dipterocarpaceae, Anacardiaceae, Bixaceae, Burseraceae, Myricaceae for dicot and Najadaceae and Typhaceae in monocot (Mole, 1993).

In conventional processes tannins are extracted from vegetable materials by using water as a solvent in a temperature range from 40^{o}C to 90^{o}C. Other organic solvents such as acetone, methanol, ethanol, ethyl acetate and aqueous solution of the same organic compounds can also be employed (Buelga and Williamson, 2003). The efficiency of solvent extraction is determined

by the type of solvent, pH, temperature, number of steps and volume of solvent and particle size in the sample. High temperature improves the efficiency of the extractions. This is because heat renders the cell wall permeable, increase solubility and diffusion coefficient of the compound to be extracted and decrease the viscosity of the solvents thus facilitating its passage through the solid substance and subsequent separating process (Ogiwara, 1980). The rate of extraction also increases along with the number of extraction steps. In this sense, it is more efficient to carry out four extraction with 50 ml of solvent than one with 200 ml. Maximum extraction is achieved when 3-5 subsequent extraction of the original plant materials are carried out (Buelga and Williamson, 2003). The pH of the extraction media determines the degree of solubility for soluble compounds and also influences the possible solubilization of the hydrolysable functions (Bickley, 1999).

There are various methods used in the detection and quantitative and qualitative analysis of tannins from plant extracts and in food and beverages (Haroun *et al*., 2013). Some of the methods used include: Hide powder method, Folins Denis method, Reverse-phase High pressure liquid chromatography (HPLC) with UV detection, Mass spectrophotometer (MS), Circular dichroism (CD), and nuclear magnetic resonance (NMR) (Buelga and Williamson, 2003, Gu *et al.,* 2003). NMR data is easily interpreted in chemical terms because each atom in a distinct environments give rise to only a single signal, the frequency and characteristics of which are predictable consequence of molecular structure and environments. Nowadays, relying upon these modern analytical techniques makes it possible to detect low molecular weight compositions of the tannins and their derivatives and provide a comprehensive understanding of their structure and chemical properties (Slade *et al.,* 2005).

2.4.1 Chemistry of vegetable tannins

Tannins are grouped into two main types, hydrolysable and condensed tannins, according to their structural feature. Condensed tannins are found in monocotyledonous and dicotyledonous plant while hydrolysable tannins are only found in dicotyledonous plants. Condensed and hydrolysable tannins can occur in the same plants (Haslam, 1981, Sikanikore *et al*., 200l). Hydrolysable tannins are types of tannin that have a molecular weight of 500-3000 Da. Hydrolysable tannins contains Gallic acid (Fig 2.1) esterified with glucose (Ali *et al*., 2013).

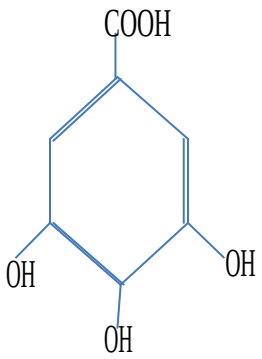

Figure 2.1: Structure of Gallic acid

Hydrolysable tannins have been further subdivided into two groups which are gallotannins and ellagitannins (Grasser, 1992). Gallotannins on hydrolysis yield gallic acid and glucose, examples of sources include: Turkish gall found on oak species and Chinese gall found on sumac species. Ellagitannins on hydrolysis give ellagic acid and glucose and example of trees that have this type of tannins are myrobalans and chestnut wood. Hydrolysable tannins have a characteristic property of undergoing hydrolysis to form `bloom`. They produce leather with a yellow or greenish cast with good light- fastness (Haslam, 1996). The color will still darken but does not acquire the redness so typical of the condensed tannins. Hydrolysable tannin contains a D-

glucose at the center of its molecules. The hydroxyl groups of the carbohydrates are partially or totally esterified with phenolic groups such as Gallic acids in Gallotannins or ellagic acid in ellagitannins (Flaherty *et al*., 1978). Hydrolysable tannins are a mixture of polygalloy glucose and/ or poly-galloyquinic acids derivatives containing between 3 up to 12 gallic acids residue per molecule (Hemmingway and Laks, 1992). Hydrolysable tannins can be extracted from different vegetable plants, such as chestnut wood, oak wood, Tara pod, myrobalams, and Aleppo gall (Haslam, 1989). Fig 2.2 shows the structure of hydrolysable tannins (Krause *et al*., 2005).

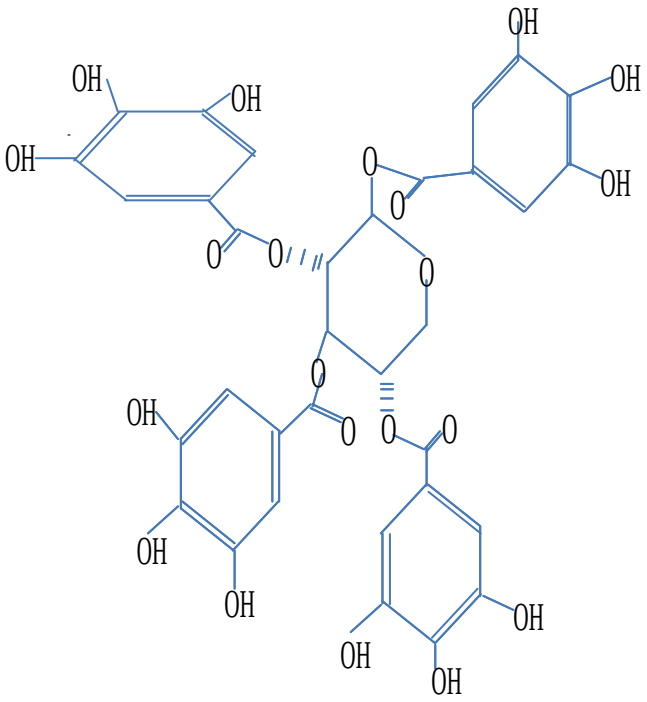

Figure 2.2: Structure of hydrolysable tannins

Condensed tannins (CT) are non-branched polymer of flavonoids units and usually have a higher molecular weight of 1000- 20000 Da than that of hydrolysable tannins (Frutos *et al*., 2004). The

typical monomer are the stereo isomeric compounds (+) - catechin (Fig 2.3) and (-) - epicatechin (Fig 2.4) (Ali *et al*., 2013).

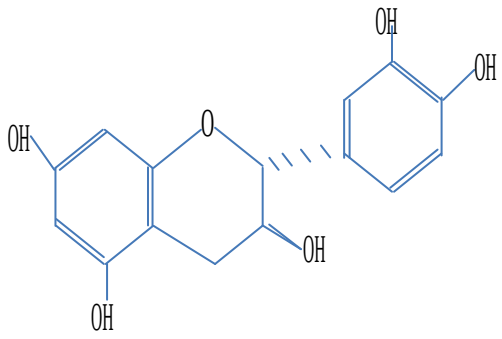

Figure 2.3: Catechin isomeric compound

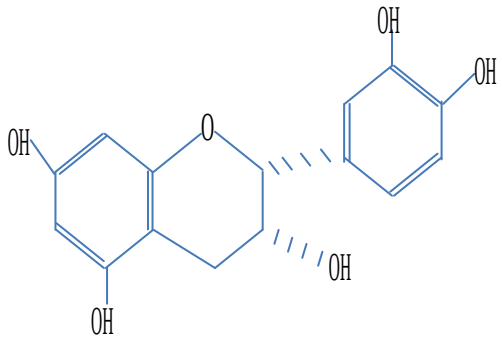

Figure 2.4: Epicatechin isomeric compound

The condensable tannins are not prone to hydrolysis but they are liable to oxidation and polymerization to form insoluble products known as 'Tannin reds/phlobaphenes' (Sanker *et al.*, 1997). They tend to be red in color (particularly on exposure to air), low in acidity, sugar and salt. Their solution is very sensitive to pH change and readily precipitated when the pH is lowered. Usually liquors made from the catechol tannins in addition to depositing less sludge

also ferment less and are less liable to mold growth than are liquors made from hydrolysable tanning materials especially chestnut and myrobalams (Sarkar, 1995). Consequently on standing, tan liquors of condensed group lose less tannin by decomposition. The commercially most important tanning materials like avaram, babul, hemlock, mangrove, mimosa and quebracho belong to this group (Reed, 2013). Condensed tannins are the most abundant types of tannins and are found virtually in all families of plants. Tannins of tropical woods tend to be of a condensed nature rather than of the hydrolysable type present in temperate woods. Fig 2.5 shows the structure of condensed tannins (Krause *et al*., 2005).

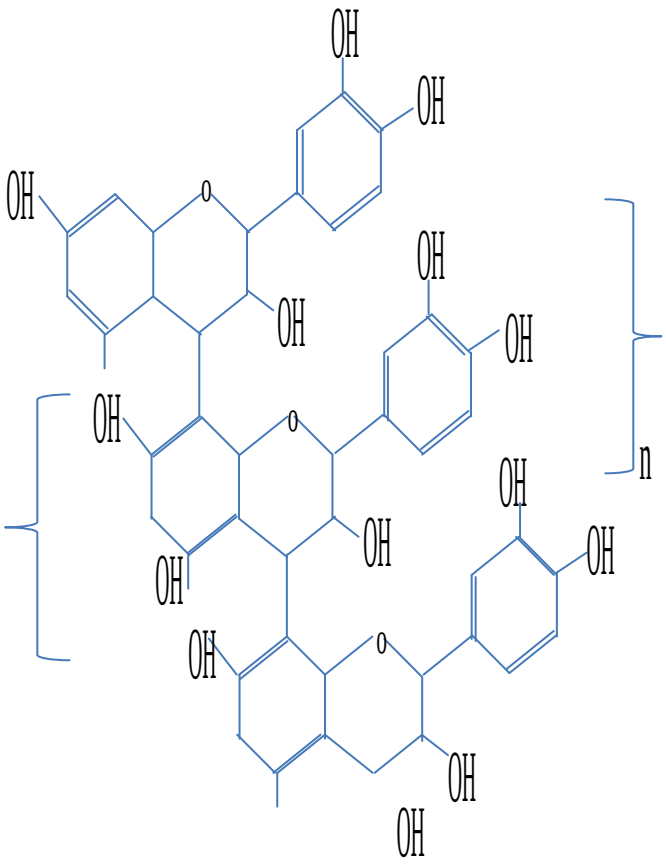

Figure 2.5: Structure of condensed tannins

During the process of leather making using vegetable tannin, the tannins binds to collagen and this makes it non-putrescible. The binding strength in tannins – protein complexes depends on the characteristics of both tannins and proteins, for example molecular weight, tertiary structure, isoelectric point and compatibility of binding sites. The affinity of tannins is higher for open and random-coiled protein rich in amino acid proline, glutamate and glycine (Hergerman *et al.,* 1992) while glycoproteins and globular proteins appear to have a lower complexation coefficient. The higher affinity of tannins to proteins is associated with the number of phenolic group that it can carry as this is the binding point to carboxyl carbon of peptide bond in protein. Therefore the higher the number of phenolic group on vegetable tannins the higher is its binding affinity to proteins (Hergerman *et al*., 1992). The higher molecular weight and flexibility in the structure of hydrolysable and condensed tannins makes it bind easily to protein with open flexible structure of the collagen (Hervey and Allan, 1992). There are four different ways in which tannins interacts with the collagen: covalent bond, ionic bond, hydrogen bond and hydrophobic bond. Among the four types of bond, only covalent bonding is irreversible. Hydrogen bond is formed between the hydroxyl radical of the phenolic group and oxygen of the amide group in the peptide bond of the proteins. This link seems to be the principal stabilizing agent of the collagen lattice. Ionic bond occurs due to the attraction of oppositely charged side groups of phenolates ions and cationic site of the protein (SLTC, 1999). Hydrophobic interaction which is dependent on pH occurs between the aromatic ring of the phenolic compounds and the hydrophobic region of the protein. Hydrophobic bond are higher at a higher ionic strength (Higher tannin/ protein ratio) and higher temperature. Covalent bonding occurs through the oxidation of polyphenols to quinones and their subsequent condensation with nucleophilic group of the proteins (Kumar and Singh

1984). Covalent bonding is far more difficult to disrupt than the previous bonding and is naturally very important because of its irreversible nature.

Vegetable tanning is essentially a two stage process (penetration and fixation) although the two stages are not completely separate, they proceed concurrently. The first stage consists of the diffusion of tannins into the collagen fibres while the second stage consists of subsequent combination of tannins with the collagen. There are several factors that affect penetration and fixation of tannins into the hides and skin during tanning process (Hergerman *et al*., 1992). These include: concentration of tannins in the tan liquor, pH, temperature, neutral salt contents, particle size and mechanical actions (Ogiwara, 1980).

In a given time, more tannin will diffuse and be fixed by the hide or skins from a liquor of high tannins content than from a liquor of low tannins content. Advantage is taken of this in the successive stages of practical vegetable tanning in the tanning systems, where penetration of the tannin is accelerated by increasing the concentration of tannins in the liquor (Sarkar, 1995). However when tanning commences with high concentration of tannins, it increases the astringencies and cause case hardening which may restrict the penetration, cause crackness or hardness of the grain. Hence, the control of the tannin concentration of vegetable tanning liquors is important. The practical tanner requires a rapid method for estimating the liquor tannin content. This is done by determining the relative density of the liquor using a special hydrometer called barkometer (Covington, 2011). This method of determining the amount of tannins can give misleading results since the relative density of the liquor is determined by the total soluble and these include tannins, non-tannins and salts.

The pH of the tanning liquor is another most important factor affecting the diffusion and fixation of tannins into the hides and skins (Ogiwara, 1980). The pH of the liquor is a measure of the hydrogen ion concentration and is determined using a pH meter, color indicator or indicator paper. The pH of the system affects penetration and fixation in various ways. Firstly reducing the pH of the tanning liquor increases the tendency of the collagen fibres to swell hence decreasing the spaces between the fibres and reduce the diffusion rate into the hide. Secondly with a decrease in acidity especially below pH 3.5 increases the tendency for tannins to combine with collagen and consequently the diffusion or penetration of the tannins into the hides or skins is further retarded because of the combination taking place between the collagen fibres and the tannins. This reduces the spaces between the fibres in addition to the restriction due to the swelling of the fibres (Reed, 2013). The types of acid used (whether a "strong" acids such as sulphuric acid or "weak" acid such as acetic acid), to acidify the tanning liquor has a marked effect on vegetable tanning. Much more of "weak" acid has to be used to acidify a tanning solution to a specific pH value than in case of a "strong" acid. Presence of salts tends to suppress the swelling of the collagen fibres especially in tannins solutions of low pH values and consequently will help increase the rate of penetration. On the other hand, excessive amounts of salts lower the degree of tannage. Hence, for proper control of vegetable tanning liquors knowledge of salt content is very important (Sarkar, 1995).

Temperature also affects the rate of vegetable tannage. Increase in temperature will increase the rate of penetration and fixation of the tannins into a hide or skin, due to the decrease in viscosity of the tanning solution with a rise in temperature. In addition an increase in temperature will increase the diffusion rate of tannin molecule and give a higher degree of tannage (Thorstensen,

1993). Control of the temperature of tanning solution is therefore important in the tanning processes. The time a hide or skin is immersed into tanning liquor, determine the amount of tannins that will diffuse and fix into the leathers. Thus it is obvious that the longer a piece of hide or skins is left in given tanning liquor, the greater will be the diffusion of the tannins into the hides or the skins, until the system reaches equilibrium. The longer the tanning reaction allowed to proceed the greater the fixation of the tannins by the collagen fibres (SLTC, 1999).

In Laikipia County, tanning of hides and skins seems to have been left in the hands of only the local tanners who use simple and outdated technologies. Some plants are preferred for tanning over others due to the level of their tannin content. Although local tanners have not tested the various plants and plant parts for their tannin contents, practical experience has shown that some plants produce better tanning agents than others; hence their persistent use in tanning by the local tanners. These vegetable tanning agents have been used for a long time. Therefore, there was a need to document information on the type and the tanning strength of vegetable tannins used by pastoral communities in Kenya.

Generally, in the tanning process an excess amount of tanning material such as tree barks, wood, fruits, pods, leaves, roots, tubers and many other plant parts are used in order to guarantee its success. For this reason, some of the tanning materials remains in residual float and are discharged as waste that threatens both environmental and human health (Song *et al*., 2000). Vegetable tannage of light and heavy leathers require 18-20% and 25-30% tannins respectively. In this research study, clean technology concept which rely on the idea that prevention is better

than reusing, reusing is better than recycling and recycling is better than discharging, will be practiced.

The natural tanning materials and their extracts are heterogeneous which means that they not only contain various kinds of tannins but also non-tannins which vary with the tanning materials themselves (Bajaj, 1998). The non-tannins consist of sugary matters, Gallic acid, soluble minerals salts and gums (Bickley, 1999).

In addition to tannins, non-tannins in vegetable tanning materials have no tanning power but their presence in the tanning liquor is important and essential to control the rate of tanning and to impact many qualities to the finished leather. The distribution of the tannins throughout the thickness of the leather and also the rate of the tanning process are largely controlled by the non-tannin content of the tanning liquor (Ali *et al*., 2013). The non-tannins affect the physical and chemical characteristics of the tanned leather. Thus leather tanned with pure gallotanin is flat, thin and lacking in fullness. On the other hand the presence of non-tannins in reasonable quantities gives soft leather with a full handle (Reed, 2013). When hides and skins are put in a tanning liquor the more astringent tanning agents get fixed into the pelt rendering the tan liquor progressively richer in non- tans. This means that the ratio of tannins to non-tannins becomes progressively lower rendering the tan liquor considerably mellower in the action. This observation led the tanners to adopt the golden rule of commencing the vegetable tanning process with old, mellow liquors and then gradually increasing the liquor strength with relatively fresh concentrated and astringent tannins.

Acid and salt in the vegetable tanning extracts greatly influence the characteristic of the leather produced. Even at lower pH of 4.0 sufficient plumping can take place if the amount of salt in the liquor is very low (Reed, 2013). The amount of acid and salt varies in different tanning extracts and the rural tanners normally adjust the amount of acid and salt content by mixing various types of tanning extracts. If the non-tannin content of the tanning materials is more than the tannins content, the tan stuff is considered unsuitable for tanning.

Since the tanning strength of a vegetable tanning material is judged based on the tannin/ soluble non-tannin ratio, various vegetable tanning materials are subjected for the analysis of tannins , non-tannins content and the pH value of the vegetable tanning liquor when determining the tanning strength of vegetable tanning materials.

2.4.2 Commonly used vegetable tanning materials

Different vegetable tanning materials have been used around the world to process hides and skins in to leathers depending on their availability and percentage of tannin concentration. Some of important plants used in tanning and their tannin concentration are chest nut 10.7%, quebracho 20%, cutch 35%, sumack leaves 25%, avaram bark 18%, bambul bark 12%, konam bark 11-14%, goran bark 26-36%, myrobalam 30-40% , wattle tree 30-40%, kahra 16%, ashan bark 12%, divi divi 35-45% tannin, sandri bark 11%, dhundri bark 28-31%, gurjan bark 35%, gorra bark and behra nuts (Wamegah, 2014, Musa and Gesmelseed, 2012, Sarkar, 1995). Laikipia County has different species of trees that can be used in leather production although their use and tannin content have not been documented. These include *Acacia nilotica, Acacia xanthophloea* and *Hagenia abyssinica. Acacia nilotica* is a spreading tree (4-5m tall) with a single-stemmed stunk

that have several branches near the soil surface. Young trees have a bark tinged with orange/ green. Mature trees have a dark rough bark and less thorny stems. The flowers are bright yellow and wattle-like. It has a spherical flower head of 1-1.2 cm in diameter. Groups of 2-6 flower heads are found at the base of each leaf joint. The tree can be used for providing fodder for the livestock and for providing shade. It can also be used as a source of fuel and as tanning materials. *Acacia xanthophloea*, also called Naivasha thorn tree is a large tree 15-25 m tall with a crown that is somewhat spreading, branching fairly up the trunk (Nundkumar and Ojewole, 2002). The barks are slightly smooth with yellow to greenish in color. Young branches and leaves of *Acacia xanthophloea* are eaten by elephant and other animals. It is also used as firewood, although it produces a gum that leaves a thick, black tar like deposit when burnt (Keith, 2010). The barks of the tree are also used in the tanning of hides and skins. *Hagenia abyssinica* is up to 20 M tall with a short trunk and thick branches. It has a thick brown or reddish brown and readily peeling bark with no thorns or buttresses. It is mostly used in timber production but can also be used as medicinal plants in control of helminthes especially tapeworm (Mekonne *et al*., 2003).

CHAPTER THREE: MATERIALS AND METHODS

3.1 Study area

This research study was conducted in Laikipia County, Kenya since it has been identified as a potential area for leather production due to high number of livestock and high production of hides and skins. There were also three groups in this county that were using different vegetable tanning material for leather production (Appendix 3). Laikipia County lies between latitudes 0^o18" and 0^o 51" North and between longitude 36^o 11" and 37^o 24' East. The County covers an area of 9,462 Km^2 and it borders eight counties namely Samburu to the North, Isiolo on the North East, Meru in the East, Nyeri to the South East, Nyandarua and Nakuru to the South West and Baringo County to the West (Laikipia County, 2013). According to the 2009 population and housing census report on livestock, there were 189,685 heads of cattle in the County and 623,648 sheep and goats. Others include poultry, camels, donkeys, rabbits and bees. The county has 50 holding grounds for livestock, two public and three private abattoirs, five auction yards and 33 slaughter slabs. In Laikipia county the current annual production of hides and skins in the county stands at 1,867 pieces and 19,000 pieces respectively all valued at ksh 29 million (Weru, 2014). Laikipia is also a range land with a ranch farming.

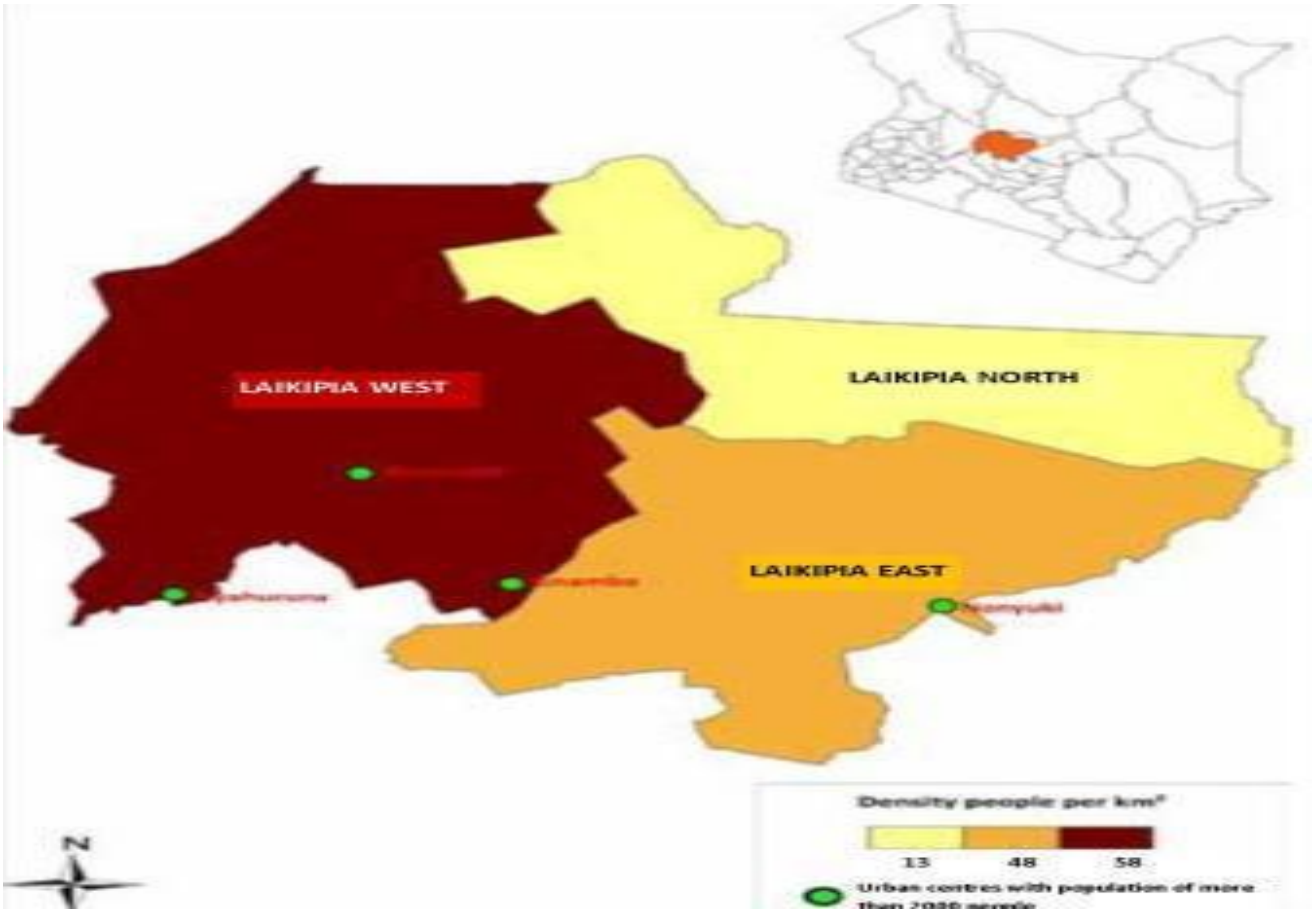

Figure 3.1 Map of Laikipia county

3.2 Sample selection and preparation

All the three groups found in Laikipia County were involved in the study. A focus group discussion was conducted on each group. The discussion majored on the types and source of vegetable tanning materials they use and the process of harvesting and preparing the vegetable tanning extracts. The discussion also involved the whole process of leather making starting from raw hides and skins to the finished leather. After the group discussion the trees species rich in vegetable tannins, which they use were identified (*Acacia nilotica* (Plate 3.1), *Acacia xanthophloea* (Plate 3.2) and *Hagenia abyssinica* (Plate 3.3)) and the samples they use were obtained from their store. Five kilograms of vegetable tanning materials (from the same species)

was obtained from each group by cutting equal sizes of the selected vegetable tanning materials and crushed to form a powder that represented the whole species of the respective plant type. The samples selected were taken to the laboratory for test analysis.

Plate 3.1: *Acacia nilotica*

Plate 3.2: *Acacia xanthophloea*

Plate 3.3: *Hagenia abyssinica*

3.3 Test for presence of vegetable tannins.

Ferric chloride test was used. One gram of powdered plant material of the test plant was weighed into a beaker and 10 ml of distilled water added. The mixture was boiled for five minutes. Two drops of 5% ferric chloride was then added. A blue or green color indicated the presence of tannins. The types of tannins were determined according to the procedure described by Jonathan, (2009).

3.4 Test for tanning strength of vegetable tannins

The hide powder method which is the official method of accurately determining the amount of tannins in vegetable tanning materials was used. Lightly chromed hide powder was used in this process. In this method, the followings were determined: moisture, total solids, total soluble, non-tannins and tannins. The pH of vegetable tannins used was also determined.

3.4.1 Hide powder preparation

The hide powder was made from ox-hide by soaking, washing in salt solution and also in distilled water. The hide was limed, bated, degreased and dehydrated with acetone and finally ground into powder by a machine (Sarkar, 1995). The recipe is in the appendix 1.

3.4.2 Chromed Hide Powder preparation

For each analysis, a multiple of hide powder containing 6.25 g of dry matter, with ten times its weight of distilled water was digested for one hour. One ml of chrome alum solution for each gram of air-dry hide powder taken was added, stirred frequently for several hours and then allowed to stand overnight. The chromed powder was transferred to clean linen, drained and squeezed. The cloth containing the powder was placed in a beaker and the cloth opened out to pour on to the powder a quantity of water equal to 15 times the weight of the air-dry hide powder. The powder and water was mixed thoroughly and digested for 15 minutes, after which the cloth and powder was removed and dried to a moisture content of 75% RH. The powder was digested three more times in the same way with distilled water. The cake of chromed powder was thoroughly broken up and mixed until uniformly free from lumps and its weight taken (BIS, 2007).

3.4.3 Determination of moistures and total solids

Five grams of finely ground vegetable tanning material was transferred into a weighing bottle and the weight taken using Laboratory analytical balance. It was dried at $100 \pm 2^{o}C$ in an oven for 3 to 4 hours, cooled in a desiccator for about 20 minutes and reweighed again. The process of

drying and weighing was repeated until two weighing at an interval of one hour did not differ by more than 2 mg (BIS, 2007).

Moisture percent by weight$= \frac{(W1-W2)\times 100}{W1}$

Total solid percent by weight$= \frac{W2\times 100}{W1}$

Where: W1= Weight in g of the material taken for test

W2= Weight in g of the residue left after drying

3.4.4 Determination of total soluble solids

Two litres of solution was extracted from a known amount of ground vegetable tanning materials using water as a solvent. One gram of kaolin was added at the base of filter paper (Whatman No.11) and the filtrate collected in a flesh beaker as soon as it became optically clear. The paper was kept full and the funnel and the collecting vessels were also covered at the time of filtration. Fifty (50) ml of the filtrate at 27± 2^{o}C was pipetted in a porcelain basin for evaporation. It was dried and weighed until a constant weight was obtained (BIS, 2007).

Total soluble solids percent by weight$= \frac{W2}{W1} \times \frac{V1}{V2}\times 100$

Where: W2= weight in gram of the residue left after dying, W1=weight in gram of the tanning materials taken, V1= volume of the test solution in ml made up originally, V2= volume in ml of the test solution taken or pipetted out.

3.4.5 Determination of non- tannins

The dry hide powder (6.25 gram) was weighed and put in a bottle of 300 ml capacity containing 100 ml of the unfiltered tannin infusion prepared. Twenty (20) ml of distilled water was then added. The bottle was closed tightly with a stopper and shaken vigorously first by hands for 15

seconds and then transferred to a mechanical rotary shaker and shaken for exactly 10 minutes at 50 to 65 rev/min. The powdered solution was poured on a clean dry linen filter cloth supported by a funnel, drained and squeezed by hand. One gram of kaolin was added to the filtrate and poured into a single 15 cm pleated filter paper until it was clear. Fifty (50) ml of the filtrate was evaporated in a tarred porcelain dish and dried in an oven at $100 \pm 2^{o}C$. It was cooled and weighed until a constant weight was observed. To correct for the 20 ml of water of dilution introduced by the wet hide powder into 100 ml of tannin solution, the residual weight was multiplied by 1.2 (BIS, 2007).

Non-tannins, percent by weight $= \frac{W2}{W1} \times \frac{V1}{V2} \times 100$

Where: W2= weight in gram of the residue left after drying, W1=weight in gram of the tanning materials taken, V1= volume in ml made up originally, V2= volume in ml of the test solution taken.

3.4.6 Determination of tannin content

The tannins content was determined by finding the difference between the percentages of total soluble solids and the soluble non- tannins (BIS, 2007).

3.4.7 Determination of pH

The pH of the solution prepared was determined by adjusting the relative density to 1.05g/ml at $27^{o}C$ with cold water, by using a pH meter (BIS, 2007).

3.5 Tanning and physical testing

3.5.1 Tanning

The vegetable tanning materials selected from Laikipia County, were sundried and ground into powder using a laboratory star mill. Particles that passed through a 2 mm sieve were used in the tanning process. In this study eight dry salted skins from a mature sheep were used. All the beamhouse processes and post tanning processes were the same for all the skins. Commercial vegetable tanning material (Mimosa) was also used for comparison purposes. The recipe used for tanning processes is in the appendix 2.

3.5.2 Comparison of Physical properties of vegetable tanned leathers

The performance of leather is dependent mainly on its physical properties. It is not possible for one test to imitate the practical action in every type of wear but it is accepted that, the test methods should provide a basis for comparison. The physical properties that were compared in leathers tanned with different vegetable tannins from Laikipia county and commercial mimosa are shrinkage temperature, tearing strength, tensile strength, grain burst test, elongation, flex endurance and grain crack.

3.5.3 Tensile strength

The tensile strength was measured using Instron 1026 according to the official method (IUP/6, 2001). The samples were cut parallel and perpendicular to the backbone using a dumbbell shaped press knife. Each sample was measured in triplicate. The jaw of the tensile machine (Instron 1026) was set 50 mm apart, and then the sample was clamped in the jaws, so that the edges of the

jaws lie along the mid line. The machine was run until the specimen broke and the highest load reached was taken as the breaking load. Tensile strength load is in Newton.

3.5.4 Shrinkage temperature determination

The shrinkage temperature of the tanned skins was measured using SATRA STD 114 test apparatus according to the official method (IUP/16, 2001). Strips of leather 50 mm × 2mm were cut from the vegetable tanned leather assessed. The specimens were cut along and across the backbone. Holes were punched at the ends of the leather to allow the specimen to be held vertically in the test chamber filled with water and a small weight was attached to the lower end. The position of the lower end was indicated by an adjustable marker outside the tube to help judge when the shrinkage occurs. The apparatus was then closed and water heated at approximately 4^{o}C by applying the external heat source to the boiler components. The temperature at which the leather started to shrink was taken as the shrinkage temperature.

3.5.5 Measurement of tear strength

The tearing strength was measured using Instron 1026 according to the official method (IUP/8, 2001). This method is intended for use with any types of leather. The different leathers were cut as a rectangle 50 mm long and 25 mm wide by use of a press knife which cuts out the specimen and slot in one operation (Template machine) parallel and perpendicular at each position. Instron 1026 having a uniform speed of separation of the jaws of 100 mm per minute was used, and the readings of load fall in that part of the scale which has been shown by calibration to be correct within 1%. The machine was run until the specimen was torn apart and the highest load reached during tearing was recorded as the tearing load. Tearing load is in Newtons.

3.5.6 Ball burst test

The ball burst test was measured using a lastometer according to the official method (IUP/9, 2001). A disc shaped specimen of the leather was firmly held with the grain side up between the clamping rings, with the spherical tip of the steel rod just touching the flesh surface. The specimen was moved downward against the rod, distending the grain of the leather immediately above the rod, while the surface is watched for incipient cracking and bursting. The force and distention values at the point at which the grain side of the leather cracked and bursted was observed and the force and distention value recorded.

3.5.7 Flexing endurance

The flex endurance test was measured using a bally flexometer according to the official method (IUP/20, 2001). Leather specimen of dimension 70×45 mm was folded and fixed to the jaws of the instrument in such a manner that the grain side remain outside with fold on the specimen. The motor was switched on when one clamp remains fixed and the other move backward and forwards causing folds in the specimen to run along it. The leather was thus flexed in the folded condition. The leather samples were flexed at 100,000 cycles and it was observed periodically for any signs of crack on the grain surface of the leather.

3.6 Data analysis

The data collected from experimental observation and results was analysed using descriptive statistics such as percentages and mean. The data was subjected to analysis using the statistical package for social science (SPSS). A student t-test was used to test the level of significant for the means tannins levels and the resultant physical properties of the vegetable tanned leathers. The $p < 0.05$ value indicated a significant difference between the means.

CHAPTER FOUR: RESULTS

4.1 Types and sources of vegetable tanning materials found in Laikipia County

Acacia nilotica, Acacia xanthophloea and *Hagenia Abyssinica* were identified as a source of vegetable tanning materials used by local tanners. The barks were the main plant parts utilized in leather production. It was also noted that, the tanners were using two different methods in tanning hides and skins. The conventional method and more environmentally friendly method called organic tanning. Although the final tanning agents for both methods are the vegetable tannins, the processes that occurs before tanning differed by using different chemicals. In conventional method, the tanners were using the chemicals commonly used in the local tanneries while in the organic method the tanners were using organic materials that are less polluting to the environment compared to the chemicals used in the conventional methods. The barks from vegetable tanning materials were first cut into smaller pieces (Plate 4.1) and put in the drum for extracting the tanning liquors. Table 4.1 shows the comparison of the two methods of leather making starting from raw skin to the finished leathers. The processing steps compared are Soaking, liming, fleshing, deliming, bating and sometimes pickling, tanning, fat liquoring and drying and they differ depending on the methods used. The percentages are based on the weight of the skins or the pelt.

Plate 4.1: Reducing the sizes of the barks

Table 4.1 Comparison between conventional and organic method of leather tanning

Processing step	Conventional method	Organic method
Soaking	They use 200% water, 2% normal detergent, and bactericide. Stirred and left overnight (24hrs.)	They used 200% water and 2% normal washing detergent. Stirred and left overnight (24 hrs.)
liming	200% water, 3% sodium sulphide, 2% lime. Stirred for one hour and left overnight	300% water, 4% fine wood ash. Stirred for several hours and left for three days
washing	The skin pelt are washed with clean water	Pelt are washed with clean water
fleshing	Mechanical fleshing	Mechanical fleshing
Deliming	200% water 2.5% ammonium sulphate, 0.5% oxalic acid. Stirred for 40 minute and left overnight	300% water, 5% wheat barley, stirred for one hour and left for two days
		Drain and washed with clean water
		100% water at $50^{o}C$, 2 sachet of cooking baking powder for 10 skins, add 2% soap and stirred for 20 minute
washing	Washed with cold water	Washed with cold water
Bating	100% water. O.5% bating enzymes	No bating
Pickling	No pickling	100% water and 5% vinegar. Stirred for 30 minutes
Vegetable tanning	Continuous addition of vegetable tanning extracts into the pelt until there is penetration throughout the cross-section of the pelt. It takes around two weeks for the tanning process to be complete	Continuous addition of vegetable tanning extracts in to the pelt until there is penetration throughout the cross-section of the pelt. It takes around two weeks for the tanning process to be complete
Fatliquoring	100% water, 7 % sulphited vegetable oil for leather manufacture, it takes around 8 hours	100% hot water, 8% vegetable cooking oils, it takes around 8 hours
Drying	Toggle drying	Toggle drying
Buffing	Done using a sand paper	Done using a sand paper
Staking	Done in order to soften the leather	Done in order to soften the leather
Ironing	Done using an iron box	Done using an iron box
Trimming	Done using a sharp knife	Done using a sharp knife

In the conventional method tanners were using the commonly used chemicals in the tanneries while in the organic method the tanners were utilizing readily available materials which are less polluting to the environment. All the three groups in Laikipia County preserve their skins using dry salted method. The skins are dry and dirty and therefore they have to undergo a soaking process. The raw skins are exposed to water and chemicals which rehydrate them to their original flaccid condition and removes, dirt, manure, blood and salts used as a preservative. Sometimes when soaking is taking a lot of time, bactericides are added to prevent proteolytic bacterial from damaging the collagen which is important in leather production. In organic tanning method the tanners in Laikipia County do not use bactericide since they believe that the chemicals used are poisonous and pollute the environment.

In the liming process, the tanners were using wood ash in the organic method compared to lime used in the conventional method. Since lime is relatively expensive and sodium sulphide is more polluting to the environment the tanners in Laikipia County are using organic method. In this method the tanners use wood ash. The wood ash is collected from homesteads around their area which is in plenty as the community use firewood as their source of fuel. The ash forms a cheap source of dehairing agent. Wood ash contains oxides and hydroxide of calcium, magnesium, potassium and to a lesser extent sodium making wood ash similar to hydrated lime in its mode of action.

In the conventional deliming method, the tanners were washing the pelt in a solution containing ammonium sulphate and ammonium chloride. In the organic method of tanning the tanners were

using wheat bran and cooking baking powder in this process. The use of wheat bran in the tanning process is called drenching.

In both the conventional and organic method, the tanners used the same procedure in preparing the tanning extract and on tanning of the skins. The tanners buy the barks in bulk and store them in a dry sheltered room. This allows the barks to dry and avoid rain which can cause leaching of the tannins hence reducing the amount of tannins in the barks. The barks are then chopped into smaller pieces and then put in a 100 litres plastic tank. When the tank was halfway full of vegetable tanning materials, cold water at room temperature was then added till the tank was full. During the tanning process the tanners took the extracts from the tank and put it into the tanning drum. If the extracts was more concentrated it was diluted with cold water before commencing the tanning process. This is because, if the tanner starts with highly concentrated tanning liquors, it will cause over tannage on the surface leading into a rough grain which is weak and brittle. Therefore the tanners started with less concentrated tanning liquors and the concentration increased subsequently. The tanners have to keep stirring the pelt in the tanning liquors in order to increase the rate of penetration. For the two methods, the vegetable tanning process normally takes two weeks. The tanners continue adding water into the drum containing the vegetable tanning materials until the color of the extracts was almost fading away. After tanning the leathers were then fatliquored with vegetable cooking oil in the organic method while in the conventional method the tanners were using sulphited oil.

4.2 Evaluation of the tanning strength of vegetable tanning materials

Since the tanning strength of a vegetable tanning materials is judged based on the tannins/ soluble non-tannins ratio of the tanning liquor, the selected vegetable tanning materials from *Acacia nilotica*, *Acacia xanthophloea* and *Hagenia abyssinica* were analysed for total solubility, soluble non-tannin (plate 4.3), tannins and pH. The tanning strength of commercial tannin (mimosa) was also determined for comparison with the vegetable tanning materials found in Laikipia County. The tanning extracts from the three plants species and mimosa are shown on plate plate 4.2.

Plate 4.2: Extracts from vegetable tanning materials

Sample for testing soluble non-tannins Sample for testing total solubility

Plate 4.3: Sample for *Acacia nilotica* ready for evaporation to get non-tannins and total solubility

The results for the total solubility, soluble non-tannins, tannins, purity ratio, tanning strength and pH of the four vegetable tanning materials are recorded in the table 4.2.

Table 4.2 Summary of the results for total solubility, non-tannins, tannins, tanning strength, purity ratio and pH

Tree species characteristics	***Acacia xanthophloea***	***Acacia nilotica***	***Hagenia abyssinica***	**Mimosa**
Moisture content %	8.9	7.1	5.9	6.9
Total solids %	91.1	92.9	94.1	93.1
Total solubility %	31	28	17.33	92
Soluble non-tannins (NT) %	7.2	11.2	5.6	29
Tannins (T) %	23.8	16.8	11.73	63
Tanning strength (T/NT) %	3.3	1.5	2.1	2.2
Purity ratio (T/TS)	0.7	0.6	0.7	0.68
Types of tannins	C	C/H	C	C
pH	4.5	5.62	4.96	4.59

KEY

C- Condensed tannins NT-Non-tannins T-Tannins

H- Hydrolysable tannins TS-Total solubility

The results indicate that there was a significant difference $p < 0.05$ in some of the properties tested between commercial mimosa and each selected vegetable tanning materials. However,

there was no significant difference in tanning strength between *Acacia nilotica* and mimosa (p=0.926), in moisture content between *Acacia xanthophloea* and mimosa (p=0.454), and pH between *Hagenia abyssinica* and mimosa (p=0.689). Table 4.3 show the p-values for comparison between commercial mimosa used as a standard with each selected vegetable tanning materials.

Table 4.3: Table of statistical analysis indicating P-values of comparison of properties tested between mimosa and three plants species (t-test)

Properties tested	***Acacia nilotica***	***Acacia xanthophloea***	***Hagenia abyssinica***
	p- values		
Moisture content	0.001	0.454	0.006
Total soluble solids	0.001	0.001	0.001
Soluble non-tannins	0.001	0.001	0.001
Tannins	0.001	0.001	0.001
Tanning strength	0.926	0.001	0.004
pH	0.001	0.001	0.689

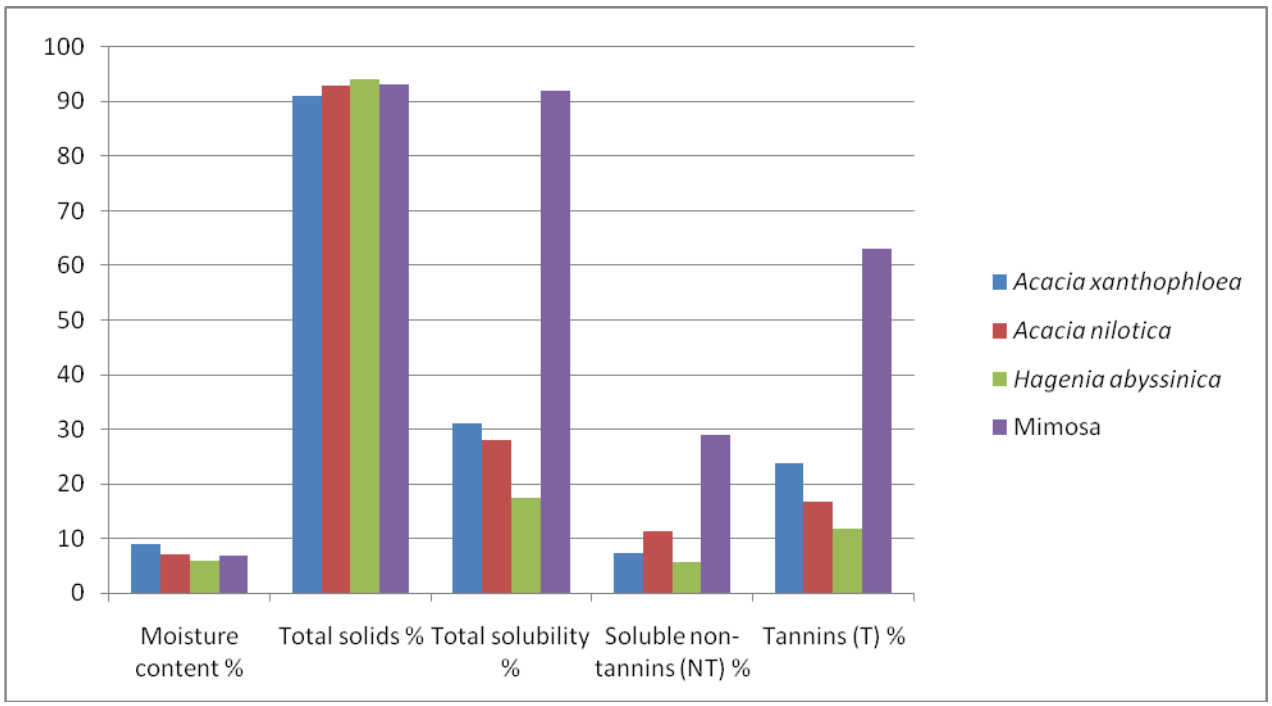

Figure 4.1: Graph showing how various components differed between the vegetable tanning materials

4.3 Comparison of the physical properties of standard mimosa and Laikipia vegetable tanned leathers

The performance of leather is dependent mainly on its physical properties. It is not possible for one test to imitate the practical action in every type of wear but it is accepted that, the test methods should provide a basis for comparison. The sheep skins from mature sheep tanned using barks from *Acacia nilotica*, *Acacia xanthophloea*, *Hagenia abyssinica* and commercial mimosa had different colors. Plate.4.4 show fatliquored, leather before it was toggle dried. The resultant leathers from *Acacia nilotica* (Plate 4.5), *Acacia xanthophloea* (Plate 4.6), *Hagenia abyssinica* (Plate 4.7), and Mimosa (Plate 4.8) had different colors and properties. Table 4.4 shows the summary results of physical properties of leathers from the four different vegetable tanning materials.

Plate 4.4: Fatliquored leather from *Acacia nilotica* before toggle drying

Plate 4.5: Leather tanned with *Acacia nilotica*

Plate 4.6: Leather tanned with *Acacia xanthophloea*

Plate 4.7: Leather tanned with *Hagenia abyssinica*

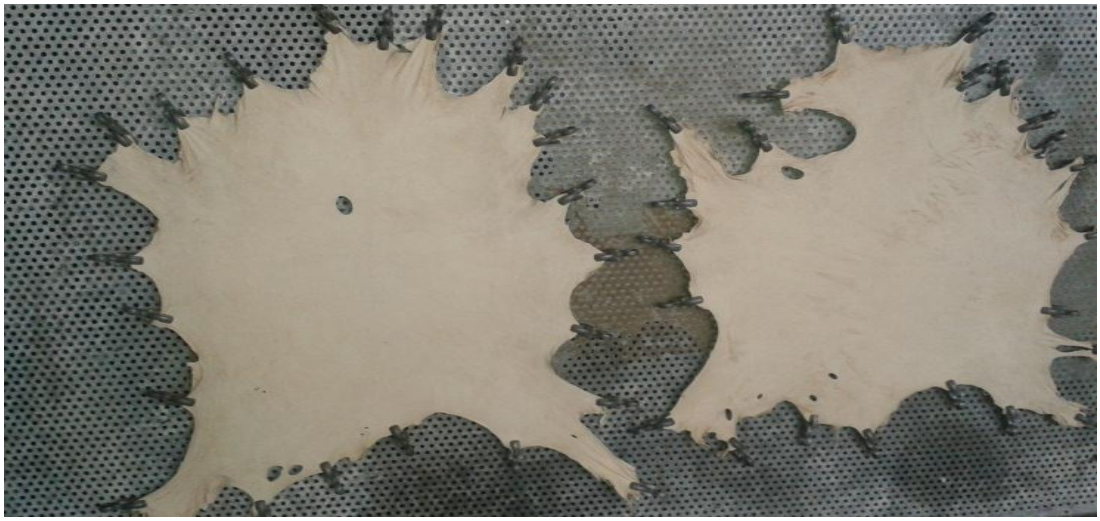

Plate 4.8: Leather tanned with commercial mimosa

Table 4.4: Physical properties of vegetable tanned leather

Physical properties		**Vegetable tanning materials**				
		Mimosa	***Acacia nilotica***	**Acacia *xanthophloea***	***Hagenia abyssinica***	**Minimum recommended value**
Ball burst extension (mm)	Grain crack	8.21±0.26	7.66±0.23	7.98±1.25	8.97±0.23	6.50
	Grain burst	8.67±0.36	8.42±0.40	8.81±0.55	9.35 ±0.34	7.00
Shrinkage temperature (^{o}C)		83	82.5	85	80	75
Flexing endurance		→No damage @ 100000	→No damage @ 100000	→No damage @ 100000	→No damage @ 100000	No damage @ 100000 flexes
		↑ No damage @ 100000	↑ No damage @ 100000	↑ No damage @ 100000	↑ No damage @ 100000	
Thickness (mm)		→0.598±0.18	→0.65±0.12	→1.003±0.12	→0.58±0.14	>0.5
		↑0.51±0.1	↑0.58±0.13	↑1.015±0.19	↑0.59±0.1	
Tensile strength (N/mm^2)		→29.92±3.83	→29.22±4.40	→19.81±2.25	→25.86±3.10	>12
		↑27.69±10.75	↑28.02±4.92	↑20.91±3.65	↑29.95±7.64	
Elongation at break (%)		→56.08±10.86	→42.4±8.89	→34.5±6.62	→43.85±2.5	>40
		↑32.83±2.32	↑38.68±7.44	↑27.83±9.87	↑37.88±4.12	
Tearing strength (N)		→34.60±11.10	→41.17±6.97	→37.17±4.88	→34.67±6.41	>20
		↑33.83±11.14	↑44.17±7.21	↑32.67±3.56	↑27.83±1.47	

KEY

↑ Leather samples cut along/parallel to the backbone

→ Leather samples cut across/perpendicular to the backbone

The physical properties of leather tanned with the selected vegetable tanning materials were compared with leathers tanned with commercial mimosa which was used as a control. The result indicated no significant difference in most of the physical properties tested between leathers tanned with commercial mimosa and each vegetable tanning materials. Table 4.5 shows the level of significant indicated by the p-values between each vegetable tanning materials and commercial mimosa.

Table 4.5: P-values for physical properties of vegetable tanned leathers (t-test)

Physical properties		***Acacia nilotica***	***Acacia xanthophloea***	***Hagenia abyssinica***
		p- values		
Ball burst extension	Grain crack	0.01	0.67	0.03
	Grain burst	0.36	0.77	0.02
Thickness		0.59	0.03	0.24
Tensile strength		0.95	0.19	0.75
Elongation at break		0.09	0.30	0.75
Tearing strength		0.15	0.59	0.99

CHAPTER FIVE: DISCUSSION, CONCLUSION AND RECOMMENDATIONS

5.1 Discussion

5.1.1 Types and sources of vegetable tanning materials found in Laikipia County

From this study, three indigenous trees were identified as a source of vegetable tanning materials. For all the three species namely *Acacia nilotica*, *Acacia xanthophloea* and *Hagenia abyssinica,* the bark was the main part of the plant used for the extraction of the tanning liquors. Although the local tanners were not aware of their tannin content, they suggested that the barks which produces deep colored liquor has more tanning chemicals compared to other plants parts. A study by Smit (2008) found that the barks from acacia species have more tannin content than other plant parts. Although there is no documentation on the use of these trees in tanning hides and skins in Kenya some have been tried in other parts of the world. A study done in Egypt found that *Acacia nilotica* is used by local people in tanning and dyeing leathers. He also noted that the extracts from the barks, leaves and pods are used for dyeing cotton, silk and leathers (Lemmences and Spetdiptoed, 1991). *Acacia nilotica* is also used widely in India and Sudan as tanning agents. Local tanners in Sudan use barks and pods from *Acacia nilotica* (Engailani and Ishak, 2014). *Acacia xanthophloea* and *Hagenia abyssinica* have not been widely used in leather production as compared to *Acacia nilotica* but their use as medicinal plants have been widely reported. A study in Ethiopia on local knowledge of plants and their use among women in Bale Mountain found that the extracts from the bark of *Hagenia abyssinica* was used for softening leathers and also used as paint (Luiza *et al*., 2013). The use of *Acacia xanthophloea* as a tanning agent has been reported in South Africa (Nundkumar and Ojewole, 2002).

5.1.2 Evaluation of the tanning strength of vegetable tanning materials

This study found the percentage tannins content of *Acacia mearnsii* extract (Mimosa) to be (63%), *Acacia nilotica* (16.8%), *Acacia xanthophloea* (23.8%) and *Hagenia abyssinica* (11.73%). There was a significant difference in the mean tannin levels between mimosa and the selected three plants (p= 0.001). The findings of this study differed slightly with findings from other studies elsewhere. For example, a study conducted in Kenya by Faggs and Mugedo, (2005) indicated that *Acacia nilotica* had a tannin content of 11-13%, while another study by Haroun *et al.* (2013) in north Sudan showed that *Acacia nilotica* had 16% tannins, 9.1% soluble non-tannins, tanning strength of 1.8 and purity ratio of 0.6. Another study by Nundkumar and Ojewole, (2002) in South Africa found *Acacia xanthophloea* barks to contain 17% condensed tannins. A study by Frutos *et al*., (2004) found *Acacia mearnsii* (Mimosa) barks extracts to have a tannin content of 63.7% and a pH of 4-6. The differences in the tannin content from the various studies may be due to the variations in the environmental factors. High temperature, water stress, extremes light intensities and poor soil quality are known to increase the tannins contents in plants. The tannins contents also vary with the bark thickness, age of the trees and from the base of the trunk upwards with the branch having low tannin contents (Donlop, 2005). The tannin content of *Hagenia abyssinica* has not been intensively studied and there was no enough data to compare with this result. This quantitative data indicate that the barks of the trees species have more than 10 % tannins required for commercial extractions (Haroun *et al*., 2013).

When the tanning strength which is the ratio of tannins to soluble non-tannins was calculated, the results showed that all the extracts from the three species had an acceptable ratio of > 0.5 with *Acacia xanthophloea* having the highest. The tanning purity (ratio of tannins/total soluble) was good for all the species. It was above the minimum recommend value of > 0.5 (Haroun *et al.,*

2013). Laikipia tanners preferred to use *Acacia xanthophloea* in the tanning process possibly because it performed better due to its higher tannin content and tanning strength compared to *Hagenia abyssinica* and *Acacia nilotica.*

All the four tanning materials contain condensed tannins while *Acacia nilotica* had both condensed and hydrolysable tannins. This concurs with the report by Sikanikore who stated that condensed and hydrolysable tannins can occurs on the same plant (Sikanikore *et al*., 200l). Condensed tannins are more preferred during tanning process compared to hydrolysable tannins. This is because condensed tannins have a higher affinity for collagen due to their high molecular weight of up to 20000 Da and a greater number of phenolic groups. These provide many points at which bonding may occur with carbonyl group of peptide (Mcleod, 1994).

The pH of their tanning liquors differed with *Acacia nilotica* having the highest pH of 5.62. *Acacia xanthophloea*, *Acacia mearnsii* extract and *Hagenia abyssinica* had a pH of 4.5, 4.59 and 4.96 respectively. The pH of the tanning liquors was within the recommended value of 4-6 for all the plant species. At pH value below 4.0 sufficient plumping of the pelt can take place if the salt contents in the liquor are very low. Plumping reduces the rate of diffusion of the tanning liquors as a result of decreasing the spaces between the fibres. Secondly, at lower pH the tendency of the tannins to combine with the collagen on the surface of the pelt increase and this lead to cranky leather with poor tannage. At pH 4-6, the leather is at its isoelectric point and the tannins can penetrate well in to the pelt and fixation takes place at a later stages.

Although the amount of tannin is very important in selecting the type of vegetable tanning materials to use, the thickness of the barks is also very important. For example, the barks of *Acacia nilotica* had a higher tannin content compared to *Hagenia abyssinica* but the plant has a thin bark and therefore a huge amount of the barks will be needed to extract enough tannin for economic feasibility unless the barks are already available.

5.1.3 Physical properties of vegetable tanned leather

In spite of the development of numerous synthetic fabrics, leather remains indispensible in many applications because of its distinct properties such as toughness, non-flammability, and resistance to heat, flexibility, impermeability to water and permeability of air and water vapor (Frederik *et al.,* 2001). In order to increase the demand for good quality leather products, quality standards have been set. Therefore the vegetable tanned leather must also be subjected to physical testing to assess their quality. The physical properties that were determined are: shrinkage temperature, ball burst test, tearing strength, tensile strength, thickness, flexing endurance and grain crack.

Shrinkage temperature is one of the most important parameters in characterizing the thermal stability of leather. It is the temperature at which the leather starts to shrinks in water or over a heating media (Ali *et al.,* 2013). It provides information about the degree of tanning because the better the crosslinking reactions between the collagen fibres and the tannins, the higher the shrinkage temperature (Heiderman, 1993). Good quality leather should have a minimum shrinkage temperature of 75^0C and all the leathers tanned with the three plant extracts had a shrinkage temperature above this expected minimum. The leather tanned with *Acacia*

xanthophloea had the highest shrinkage temperature of 85^{o}C compared with the leather tanned with commercial mimosa (83^{o}C), *Acacia nilotica* (82.5^{o}C), and *Hagenia abyssinica* 80^{o}C.

From the results obtained from this research *Acacia xanthophloea* had the highest tanning strength of 3.3 and this might also be the reason for its highest shrinkage temperature. Research by Covington showed that leathers tanned with condensed tannins have a shrinkage temperature of more than 80^{0}C. He concluded that an observed shrinkage temperature of $>$ 80^{0}C is a strong indication that the condensed tannins have been used in a tanning process (Covington, 2011).

Tensile strength of leather is the greatest longitudinal stress leather can bear without tearing apart. The tensile strength of leather is determined by the fibrous structures that constitute the collagen network structure and the modification of this structure by the tanning agents (Covington, 2009). Good overall tensile strength value of leather varies depending on the types of the tannins applied to them and the application levels (John, 1997). The tensile strengths of the leathers tanned by all the three vegetable materials in this study were way above the expected minimum of 12N/mm^{2,} and were comparable to the tensile strength of leathers tanned with *Acacia mearnsii* extract. A study done in Ethiopia on the leather quality of indigenous and cross breed sheep reported an average tensile strength of 24.36 N/mm^{2} (Teklebraham *et al*., 2012) which was comparable to the findings of this study.

The small variation in tensile strength of the leathers produced by tanning with the three study vegetable tanning materials was due to difference in the thickness of the leathers. The leather from *Acacia xanthophloea* was thicker than the others. This difference in thickness may be due

to low pH in the tanning extracts of *Acacia xanthophloea* as compared to other tanning agents used. Lower pH and low salt content in the tanning liquors are known to cause plumping of the leathers (Sarkar, 1995).

The percentage elongation of leather is another physical property measured when assessing the leather quality and this has a relationship with the tensile strength. Elongation refers to the ability of a leather product to lengthen/stretch when stress is applied to it and represents the maximum extent leather can stretch without breaking. Elongation is an important property to be considered when choosing garment leathers because a low elongation value results in easy tear while a high elongation value causes leather goods to become deformed very quickly or even loose usability (Ork *et al.,* 2014). Leathers that have a lower tensile strength have a lower percentage elongation and vice versa. Good quality leathers should have a percentage elongation of $\geq$ 40% (Roigi, 2012). In this study, it was observed that leathers tanned with *Acacia xanthophloea* had the lowest percentage elongation (31.17 %) compared to commercial extract from *Acacia mearnsii* (44.82%), *Acacia nilotica* (40.54%) and *Hagenia abyssinica* (40.87%). A study in Ethiopia on the performance of leather uppers of local foot wear products and determinant observed an elongation of 13.6% (Ashebre, 2014). This low performance in percentage elongation emphasized that the leather has no enough elasticity required for making shoes uppers. Another study by (Teklebraham *et al*., 2012) found the sheep skins leathers to have an elongation of 48.1%. Elongation of leathers is affected by pre-tanning, tanning and post tanning process which always differs from one tanner to another.

The strength of the leather products in use is indicated by the quality standard relating to tearing load. The minimum tearing strength should be at least 20N (Anonymous, 2007). This study found the tearing strength of all the vegetable tanned leathers studied to be higher than 20 N with *Acacia nilotica* having 42 N, *Hagenia abyssinica* 31 N, *Acacia xanthophloea* 34.92 N and *Acacia mearnsii* extract 34.22 N. A comparison of the tearing strength of leathers tanned with commercial *Acacia mearnsii* extract indicated no significant difference with leathers tanned with *Acacia nilotica* (p= 0.15), *Hagenia abyssinica* (p= 0.99) and *Acacia xanthophloea* (p= 0.59). This is comparable to a study by (Ashebre, 2014) which found the tearing strength of sheep skins leathers to be 28 N. The type of tanning materials and the beamhouse processes are some of the factors known to affect the tearing strength of leather (Basaran *et al*., 2006).

The ball burst test is another physical property for testing quality of leathers. It is intended to indicate the grain resistance to cracking during top lasting of the shoe uppers. All the leathers tested had more than 6.5 mm and 7.0 mm the minimum recommended value for grain crack and grain burst tests respectively. The grain crack value for *Acacia nilotica* was 7.66 mm, *Hagenia abyssinica* 8.97 mm, *Acacia xanthophloea* 7.98 mm and *Acacia mearnsii* extract 8.21 mm. while the grain burst for *Acacia nilotica* was 8.42 mm, *Hagenia abyssinica* 9.35 mm, *Acacia xanthophloea* 8.81 mm and *Acacia mearnsii* extract 8.76 mm. There was no significant difference in the mean grain crack (p=0.67) and grain burst (p=0.77) value between *Acacia mearnsii* extract and *Acacia xanthophloea*. The p value for comparison between *Hagenia abyssinica* and leathers tanned with *Acacia mearnsii* extract was lower indicating a significant difference in grain crack (p=0.03) and grain burst (p=0.02) test. For *Acacia nilotica*, there was a significant difference in grain crack (p=0.01) but no significant difference in grain burst test

(p=0.36). Various studies have found different value for grain crack and grain burst tests for sheep skins tanned leathers. For example, grain crack of 6.74 mm and a grain burst test of 7.72 mm (Lawal and Odums, 2015), grain crack of 9.9 mm and grain burst of 10 mm (Teklebrham, 2012), grain crack of 10 mm and grain burst of 10 mm (Ashebre, 2014). The breed of the sheep, pre-tanning, tanning and post tanning processes are known to affect the grain crack and grain burst test which vary from different tanners (Selehl *et al.,* 2013).

Flexing test is normally done on the leathers intended for making shoes or products that flex several time (UNIDO, 1994). Flexing test was applied to the respective leathers and there was no damage at 100,000 flexes to any of the leathers. All the study leathers passed the flexing test. A study on vegetable tanned leathers finished with polyvinyl alcohol failed the flexing test at 20,000 flexes while the leathers finished with nitrocellulose did not show any effect at 20,000 flexes (Gumel and Dambatta, 2013). When leathers was flexed several times as in the case of ramp portion of the shoes, bellows and portfolios, the free grease was pushed away from the flexed region causing the leather to crack at that particular point. Heavy retanning and type of finishing affect the flexing endurance of the leather (Gumel and Dambatta, 2013).

5.2 Conclusion

- The bark from *Acacia nilotica*, *Acacia xanthophloea* and *Hagenia abyssinica* were identified as a source of vegetable tanning materials used by rural tanners in Laikipia County.
- The percentage tannins content of *Acacia nilotica* was 16.8%, that of *Acacia xanthophloea* was 23.8% and *Hagenia abyssinica* was 11.73%. All the three species have potential for commercial exploitation.
- The tanning strength of the three vegetable tanning material was more than the minimum recommended value of 1.5, while the purity ratio was above the minimum recommended values of 0.5
- The leathers tanned with *Acacia nilotica*, *Acacia xanthophloea* and *Hagenia abyssinica* were of comparable quality with that of *Acacia mearnsii* extract (Mimosa) tanned leathers and they all passed the minimum set standards for good quality leather.

5.3 Recommendation

- The high tannins content in the barks of *Acacia nilotica, Acacia xanthophloea* and *Hagenia abyssinica* growing in Laikipia County should be exploited for commercial use in leather tanning.

REFERENCES

Ali, S.D., Haroun, H.E and Musa, A.E. (2013). Haraz bark powder extracts for manufacture of Nappa upper leather as alternatives retanning agents. *Journal of Forest Production and Industrie*s, 2(5)25-29, ISSN: 2325-4513 (PRINT) ISSN 2325-4513X (ONLINE).

Anonymous, (2007). Pocket book for the leather technology. BASF publisher. P70-80.

Ashbre, M (2014). Performances of upper leathers of local foot wear products and the determinants. *International Journal of Advancements in Research and Technology*, 3: ISSN 2778-7763

Bajaj, Y. P. S. (1988). Medicinal and Aromatic Plants. *Biotechnology in Agriculture and Forestry* 24. Berlin: Springer-Verlag. ISBN 0-387-56008-4.

Bassaran, B., Iscam, M., Bitlisii, B. and **Asian, A. (2006**). Heavy metal content of various finished leathers. *Journal of the Society of Leather Technology and Chemist* **90**: 229-234

Bickley, J.C. (1999). Vegetable tannins and tanning. *Journal of Society of Leather Technologist and Chemists*, 76, 1.

Bielicila, A., Bojanowiska, I and Wisniewsk, (2005). Two faces of chromium-pollutant and Bioelement. *Polish Journal of Enviromental Studies*. **14**: 5-10

Boren, J., Terrel, T., Brian, J., Hurd and Mason G, (2009). Tanning deer hides and small fur skins. Guide L-103

Bryant, J.P., Reicharit, B.P. and Clausen, T.P. (1992). Chemically mediated interactions between woody plants and browsing mammals. *Journal of Range Management*, **45**, 18-27.

Buelga and Williamson, (2003). Methods in polyphenols analysis, The Royal Society of Chemist publisher, Page 1-5.

BIS, (2007). Methods of test for vegetable tanning materials. Doc: CHD17 (1627) C

Covington, A.D. (2009). Tanning chemistry: the science of leather, The Royal Society of Chemistry, Cambridge volume 10, 95-105

Covington, A. (1997). "Modern Tanning Chemistry," Chemical Society Review 1997, volume 26, 111–126. Doi:10.1039/CS9972600111.

Covington, A. (1997). Future tanning chemistries.www.leathermag.com/features/feature...

Covington, A. (2011). Tanning chemistry, the science of leather. Published by the Rayal Society of chemists, Cambridge CB4, UK Page 881-314. ISBW: 978-1-84973-434-9

Donlop, R.W. (2005). Acacia mearnsii De wild in: Jansen, P.C.M and Cardon, D. Editors (PROCTER 3: Dyes and tannins/ cororants tanins.){CD-ROM}. PROTA, Wagenigen, Netherland

Eldin, I., Hussein E. and Christina, Y.I (2014). Determination of tannins of three common Acacia species of Sudan. *Journal of Advanced in Chemistry*, **9:**25-30

Engailani, I. E. and Ishak C. Y. (2014). Determination of tannins of three common Acacia species of Sudan. *Journal of Advances in Chemistry*, **5:**45-53

Etherryton and Robberts, (2011). Foundation of American institute for conservation. https//en.wikipedia.org/wiki/tannin. Retrieved 2015

Faggs, C.W and **Mugedo, J. (2005**). Acacia nilotica (L) Wild.exDelilein: jansen, P.C.M and Cardon, D. Editors (PROCTER 3:Dyes and tannins/ cororants et tanins.){CD-ROM}. PROTA, Wagenigen, Netherland.

Faxing, L., Yang, L. and **Youjie, H. (2005)**. Preparation and the Properties of Vegetable Extract Used in Low Temperature Tanning . *Journal of Leather Science and Engineering* **15**(1): 22-26

Flaherty, F.O., Roddy, W. and Lollar, R.M. (1978). The chemistry and technology of leather. Robbert E.Krieger Publishing CompNY Malabar, Florida.page 387-458.

Flederick, H., Romer, A.U., Nadine, S., Susan, l., Bonnet, M.D., David, R. and **Dan, V. (2001).** Tanning fingerprint in vegetable tanned leather by solid state NMR spectroscopy and comparison with leather tanned by other processes.**16**: 1240-1252

Frutos, P., Hervas, G., Giraldez and Matelon, A. (2004). Tanning and ruminant nutrition. *Spanish Journal of Agricultural Research*, **2**: 191-202

Grasser, G. (1992). Synthetic Tannins. F. G. A. Enna. (Trans). Page 13, ISBN 9781406773019

Gu, l., Kelm, M. A., Hammerstone, J.F., Zhangz,. Beecher, G., Holden, J., Haytowitz, D.J and Prior R.L. (2003). Liquid chromatographic/ electrol spray ionization mass spectrometric studies of proanthocyanins in foods. *Journal of Mass Spectrum*, **38** 1272-1280

Gumel, S.M., Dambatta, B.B. (2013). Application and evaluation of the performance of polyvinyl alcohol and it's bled with nitrocellulose in leather top coating. *International Journal of Chemical Engineering and Applications*, **4**:4-8

Habib, A.B., Noor, L.A, and A.E Musa (2015). Effect of some skin defects on physical properties of leather. *Journal of Applied and Industrial Science*.**3**:112-119

Haroun, M., Palmina, K. and **Covington, T.(2013)**. Evaluation of vegetable tannin contents and polyphenols of some indigenous and exotic woody plant species in Sudan. *Journal of Forest Products & Industries*, **2**:48-54

Haroun, M., Palmina, K. and **Covington, T. (2009)**. Potential of vegetable tanning materials and basic Aluminium sulphate in Sudanese Leather industry. *Journal of Engineering Science and Technology*, **4**: 20-31

Haroun, M., Palmina, K. and **Covington, T. (2013**). Analysis of commercial vegetable tannins materials and related polyphenols of selected Acacia species in Sudan. *Journal of Forest and Industries*, **2**(1):21-28. ISSN: 2325-45-13(PRINT) ISSN 2325-453X (ONLINE)

Haslam, E. (1981). Vegetable tannins, the biochemistry of plant, vol.7 academic press, New York pp.527-554

Haslam, E. (1989). Plant Polyphenols, Vegetable Tannins Revisited. Cambridge University Press, Cambridge, Uk. Pg.64-100

Heidemann, E. (1993). Fundamentals of Leather Manufacture. Eduard Roether KG. p. 211. ISBN 3-7929-0206-0

Hergerman, A.E., Robbins, C.T., Weeradurigas, X.J., Wilson, T.C. and **Arthur, M.C. (1992**). Tannins chemistry in relation to digestion. *Journal of Range Management.***45**: 4-50

Hemingway, R.W. and **Laks, P.E. (1992)**. Plant Polyphenols: Synthesis, Properties and Significance. Springer publisher, page 30-40

Hervey, M. and Allan, B. (1992). Tannins, their biochemistry and nutritional properties in plant cell. *Biochemistry and Biotechnology*, Vol 1. JAL press Ltd., London (UK) pg. 151-217

International Union of Leather Technologist and Chemist societies (2001) IUP/6: "Measurements of tensile strength and percentage elongation". Society of Leather Technologist and Chemists.

International Union of Leather Technologist and Chemist societies (2001) IUP/8: "Measurements of tearing strength". Society of Leather Technologist and Chemists.

International Union of Leather Technologist and Chemist societies (2001) IUP/9: "Measurements of distention and strength of grain by the ball burst test". Society of Leather Technologist and Chemists.

International Union of Leather Technologist and Chemist societies (2001) IUP/16: "Measurements of shrinkage temperature up to 100^{o}C". Society of Leather Technologist and Chemists.

International Union of Leather Technologist and Chemist societies (2001) IUP/20: "Measurements of flex resistance by flexometer method". Society of Leather Technologist and Chemists.

Jianzhong, M.A., Yun, L., Bin, L., Dangge, G. and Likun, W. (2009). Synthesis and properties of tannin/ vinyl polymer tanning agents

John, G. (1997). Possible defects in leather production. Druk partners Rubeimann, Hemsbach page 4-10

Jonathan, Y. (2009). Phytochemical analysis and antimicrobial activity of scoporia dulus and nymphaea lotus. *Australian Journal of Basic and Applied Science*. **3**: 397-3979

Kaith, D.C. (2010). Informal technical report on forestry of tanning bearing trees crops. FAO, Rome. *Journal of Tropical Forest Science* **18** (3): 181-187

Kaloka, O. and **Moreki** (2011). Tanning hides and skins using vegetable tanning agents in Hukuntsi sub-district, Botswana. *Journal of Agricultural Technology*, **7**(4) 915-922.

Khanbabaee, K., and **Van, R., (2001).** Tannins: classification and definition, Nat. Prod. Rep. 18 641–649. Hoboken

Kitney, M. (2011). Sensible Survival: Making raw hides https//en.wikipedia.org/tanning wikipedia. Retrived 2015

Krause, D.O., Smith, J.M., Brouler, J.D and Sweeney, C.S (2005). Tolerance mechanism of streptococci to hydrolysable and condensed tannins. *Journal of Animal Feed Science and Technologies* **121:** 59-75

Kumar, R and Singh, M (1984). Tannins, their advance role in ruminant nutrition. *Journal of Agricultural and Food Chemistry,* **32**,447-453

Laikipia County, (2013). First County development integrated development plan 2013-2017. Page 5-33

Lawal, A. S and Odums (2015). Tanning of different animal skins / hides and study of their properties for textile applications. *British Journal of Applied Science and Technology*, **6**: 588-594

Larkin (2013). Flora and Fauna: The Mpala Research Center and the Impala Wildlife Foundation. http://www.larkinheather.com

Lemmences, H.M., and Spetdiptoed (1991). Dye and tannin producing plants: plant resource of south East Asia. Page1-3

Markcurtis, (2010). Developing the leather sector in Kenya through export taxes. The benefits of defying the EU, Oxfarm publisher, Germany pg. 1-5

Marion, K. and **Roy, T. (2006**). Conservation of leather and related materials. Butterworth-Heinemann.pg. 23.ISBN 978-0-7506-4881-3

Mathew, W.l., Heather Y.C., Paul, E., Aserat W., Rainer W and Amber Weimer (2013). Local knowledge of plants and their uses among wemen in the bale mountains, Ethiopia. *Journal of Forestry Research* **6**: 12-35

Mcleod, M.N. (1994). Plant tannins- their role in forage quality. Nutr. Abst Rev **44**,803-812

Mekonnen, K., Glatzel G.and Sieghardit M. (2003). Assessment of Fodder Values of 3 Indigenous and 1 Exotic wood plant species in the Highland of Central Ethiopia. *Journal of Mountain Research and Development*. **24**-112-123

Mole, (1993). "The Systematic Distribution of Tannins in the Leaves of Angiosperms: A Tool for Ecological Studies". *Biochemical Systematics and Ecology* **21** (8): 833–846. doi:10.1016/0305-1978(93)90096-A

Moorthy, M. and Mekonnen (2013). Preparation of Eco-friendly leather by process modification to make pollution free tanneries. *Journal of Engineering, Computer and Applied Science*, Volume 2 p.5

Musa, A.E., and Gesmelseed, G.A. (2012). Characterization of Lawsonia inermis as vegetable tanning materials. *Journal of Forest Products and Industries*, **2**:35-40

Mwinyihija, M., Strachan, J., Dawson, J., Mehang, A. and **Kilham, k. (2006**). An eco-toxicological Approach to assessing the impacts of tanning industries effluent on river health. *Arch Environs Contam Toxicol* **50**:316-324

Mwinyihija, (2010). Hides, Skins and Leather value addition initiative, the Kenyan scenario, held at Nairobi Safari Club, Mawingu Conference Room, on 23rd -25th.

Nundkmar, N. and Ojewole, J.A. (2002). Studies on the antiplasmodial properties of some South Africa medicinal plants used and antimalaria remedies in folk medicine. *Journal of Pharmacology*, **24**: 397-402

Ogiwara, C. (1980). Practical guide to leather processing, Tokyo Japan Ferozsons printers Ltd. Page 103-123

Ork, H., Ozgumay., Mehmet, M.M. and **Ziymet., O. (2014**). Comparative determination of physical and fastness properties of garment leathers tanned with various tanning materials for the leather skirt production. **31**:20-30

Plavan, V., Valeika, V., Kovtunenko, O. and Širvaitytė, J. (2009). The Pretreatment before Tanning (Chrome or Nonchrome). J*ournal of the Society of Leather Technologists and Chemists* **93**:186 – 192.

Raghara, R.J., Chandrobabu ,N.K., Muralidharans, C., Unni Nair, B., Rao, P.G. and **Ramasami, T. (2003);** Recouping the waste water: Away forward for clean leathers processing. *Journal of Cleaner Production,* **11**: 591.

Ramasami, T. and **Prasad (1991)**. Environmental aspects of leather processing. *Proceeding of the LEXPO-XV,Calcutta,* india,pp43

Reed, R (2013). Science for students of leather technology, pergamon press, pg. 30-240

Rohner, C.S., and **Ward, D (1997**). Chemical and mechanical defense against herbivore in two sympathetic species of desert acacia. *Journal of Vegetable Science* **8**: 717-726

Roigi, M., Segarral,. V. Martinazi, M.A., Ferreri, J. and **Raspiz, C. (2012**). Chrome free leathers, tanned with oxixalidine. *Journal of Aqueic* **63**:50-60.

Sah, N.K, (2013). Greener approach to leather techniques. Thesis of the University of Applied Science, Degree programme in chemistry and technology. Page 1-18

Santos, L.M and Gutterres, M (2006). Reusing of a hide waste for leather fat liquoring. *Journal of Cleaner Production*.**15.**12-16

Sarkar, K.T. (1995). Theory and practice of leather manufacturer 4th Edition, Revised publisher pg. 201-224

Seigler.D (2005). Integrative Biology, plant and their uses, USA. 217:333-7577

Selehl. M, Lavvat, A and Farahvash T (2013). Skin quality and physical properties of leather based on sex, age and body parts of goat reared on sub-humid hill country. *Iranian Journal of Applied Animal Science,* **3**: 853-857

Sikanikore, N., Perevolotstive, A. and Provenza, F.D, (2001). Use of tannin-binding chemicals to assay for tannins and their negative postigestive effects in ruminants. *Journal of Animal Feed Science and Technology*.**91**:69-81

Slande, D., Ferreira, D.J, Marais, J.P (2005). Circular dichroism, a powerful tool for the assessment of absolute configuration of flavonoids. *Photochemistry* **66**:2177-2215

SLTC, (1999). Society of Leather Technologist and Chemists Pocket book. SLTC publisher, East Yorkshire, UK page 72-73.

Smit, N. (2008). Field Guid to the Acacia of South Africa. Briza publications Pretoria. Page 1-5

Song, Z.,Williams, C.J. and Edyvean, R.G (2000). Sedimentation of Tannery Waste water. *Water Research*, **34**(7), 2171-2176,

Souza, F.R and Gutterres, M. (2012). Application of enzyme in leather processing: A comparison between chemical and coenzyme processes. *Brazilian Journal of Chemical Engineering*, **29**(3): 473-481

Tegtmeger, D and Kleban, M. (2013). Chrome and leather research, a balanced view of scientific facts and figures. International Union of Leather Technologist and Chemist Societies

Teklebrham, T. , Mengistu U. and Yoseph, M (2012). Skin/ Leather quality of indigenous crossbreed F1 sheep. *Livestock research for Rural Development*, **24:**4-8

The world Book Encyclopedia L Volume 12, (2001). World Book, Inc a Scott Fetzer Company, Chicago. (pp. 166-169)

Thorstensen, T. (1993). Practical leather technology. 4th edition, Krieger publisher company Malabar, Florida: ISBN 0-89464-689-3 pg-147-171

UNIDO, (1994). Acceptable quality standards in the leather and foot wear industries. Page 15

Vest, M. (1999). White tawed leathers- aspects of conservation. Preprint from the 9th International Congress of IADA, Copenhagen 15-21,

Wamegah, R. (2014). Vegetable tanning in Bolgatanga: Challenges and the way forward. *Journal of Arts and Design Studies*, **16:27**-31

Weru, (2014). Laikipia County an oasis of opportunities. Standard paper Friday, April

Yapici, B. M., Yapici, A.N. and Kecici, E.C. (2008). The effect of reuse of unhairing-liming residual floats through regeneration on the microorganism number. *African Journal of Biotechnology*. **7**:3077-3081

Young, T.P., Okello, B.P., Kinyua D. and **Palmer, T.M. (1998**). A long thorn multispecies herbivore exclusion experiment in Laikipia, Kenya.*African Journal of Range Forage Science*.**14:**94-102

APPENDICES

Appendix 1: Recipe for process steps (hide powder preparations)

Operations	Products	%	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 (12.00)
Deliming	Ammonium sulphate Oxalic acid	2.5% 0.5%	Run for 40 min 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 process steps (Tanning process)

Operations		products	%	Run time	remarks
soaking	Washing/dirt soak	Water at 20°C Detergent	200% 1%	20 min	
	Main soak	water	200%	4 hrs	
Drain and wash with clean water					
Unhairing and liming		Water @ 20°C sodium sulphide Lime	150% 1.5% 1%	1hr	
add		Water @ 20°C sodium sulphide Lime	50% 1% 2%	8hrs	pH≥ 12.0
Drain and wash with clean water					
Fleshing and scudding					
Deliming		Water @ 20°C Ammonium sulphate Sodium metabisulphite	150% 2% 1%	1 hr	Check pH of the cross-section with phenolphthalein (8.0-8.2)
Drain					
Bating		Water @ 35°C Bate powder	100% 1%	1 hr	
Tanning		Water @ 30°C Vegetable tanning materials	150% 5%	5hrs	Check penetration
Add		Vegetable tanning materials	3%	5hrs/ leave overnight	Checks pH (4.0-6.0) Check penetration
Fixation		Formic acid	1%	1hr	pH. 3.5
Drain and wash					
Leave overnight for aging					
Fat liquoring		Warm water Fat liquoring	100% 7%	2hrs	
Fixation		Formic acid	1%	1hr	Check pH. 3.5
Drain and wash					
Horse up overnight					
Toggle drying					

Appendix 3: Composition of focus group discussion

Name	**location**	**Number of people**	**Tanning material used**
Ngare narok group	rumuriti	10	*Acacia xanthophloea* *Acacia nilotica* *Hagenia abysinica*
Mr saitoti group	Near rumuruti	5	*Acacia xanthophloea* *Acacia nilotica* *Hagenia abysinica*
Mr. Kariuki group	Near nyahururu	**8**	*Acacia xanthophloea* *Acacia nilotica* mimosa

Appendix 4: Tables of statistical tests

Paired Samples Test for percentage total tannins

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	H.Abyssinica - A.nilotica	4.62000E1	.30000	.17321	45.45476	46.94524	266.736	5	.000
	Mimosa-A.xanthopholacea	3.9200E1	.17321	.10000	38.76973	39.63027	392.00	5	.000
	Mimosa-H.Abyssinica	5.1270E1	.12530	.07234	50.95874	51.58126	708.719	5	.000

Paired Samples Test For Tensile Strength

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Mimosa - A.nilotica	-.33500	12.92774	5.27773	-13.90184	13.23184	-.063	5	.952
	Mimosa-A.xanthopholacea	6.79167	11.09248	4.52489	4.84918	18.43251	1.500	5	.194
	Mimosa-H.Abyssinica	-2.27167	17.06830	6.96810	-20.18375	15.64041	-326	5	.758
	→ Across the backbone								
	Mimosa - A.nilotica	-.09500	4.24277	2.12139	-6.84619	6.65619	-.045	3	.967
	Mimosa - A.xanthopholacea	1.03740E1	4.03148	1.80293	5.36826	15.37974	5.754	4	.005
	Mimosa - H.Abyssinica	4.06000	3.07574	1.37551	.24096	7.87904	2.952	4	.042

Paired Samples Test for thickness

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Mimosa - A.nilotica	-.07000	.15582	.06361	-.23352	.09352	-1.100	5	.321
Pair 1	Mimosa - A.xanthopholacea	-.50333	.25406	.10372	-.76995	-.23671	-4.853	5	.005
	Mimosa - H.Abyssinica	-.08000	.14846	.06061	-.23580	.07580	-1.320	5	.244
→ Across the backbone									
	Mimosa - A.nilotica	-.05167	.22498	.09185	-.28777	.18444	-.563	5	.598
	Mimosa - A.xanthopholacea	-.40500	.19087	.07792	-.60530	-.20470	-5.198	5	.003
	Mimosa- H.Abyssinica	.01833	.27694	.11306	-.27230	.30897	.162	5	.878

Paired Samples Test for elongation

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Mimosa - A.nilotica	-2.90000	3.40823	1.39140	-6.47671	.67671	-2.084	5	.092
	Mimosa-A.xanthopholacea	2.50000	5.31865	2.17133	-3.08158	8.08158	1.151	5	.302
	Mimosa-H.abyssinica	2.46667	2.16764	.88494	-4.74147	-.19187	2.787	5	.075
	→ Across the backbone								
	Mimosa - A.nilotica	6.84000	5.44913	2.43692	.07401	13.60599	2.807	4	.048
	Mimosa - A.xanthopholacea	1.16000E1	6.78565	3.03463	3.17451	20.02549	3.823	4	.019
	Mimosa - H.abyssinica	6.20000	5.80818	2.59750	-1.01181	13.41181	2.387	4	.075

Paired Samples Test for grain crack

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Mimosa - A.nilotica	5.70000E1	37.28270	15.22060	17.87420	96.12580	3.745	5	.013
	Mimosa-A.xathopholacea	2.1166E1	114.28109	46.65506	-98.76398	141.09731	.454	5	.669
	Mimosa-H.abyssinica	-7.633E1	35.25148	14.39136	-113.32749	-39.33918	-5.304	5	.003

Paired Samples Test for grain burst

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Mimosa - A.nilotica	2.53333E1	61.79212	25.22653	-39.51352	90.18019	1.004	5	.361
	Mimosa-A.xanthopholacea	-5.00000	39.62323	16.17611	-46.58203	36.58203	-.309	5	.770
	Mimosa-H.abyssinica	-7.233E1	57.41661	23.44023	-132.58837	-12.07830	-3.086	5	.027

Paired Samples Test for tearing strength

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Mimosa - A.nilotica	-6.56333	9.33247	3.80997	-16.35716	3.23050	-1.723	5	.146
	Mimosa-A.xanthopholacea	-2.5633	11.85871	4.51470	-14.16874	9.04207	-.568	5	.595
	Mimosa-H.abyssinica	.06333	15.94701	6.51034	-16.79869	16.67203	-.010	5	.993
↑ Along the backbone									
	Mimosa - A.nilotica	-1.03350E1	11.23332	4.58599	-22.12365	1.45365	-2.254	5	.074
	Mimosa - A.xanthopholacea	.99833	11.06572	4.51756	-10.61443	12.61110	.221	5	.834
	Mimosa - H.abyssinica	5.99833	12.54617	5.12195	-7.16806	19.16473	1.171	5	.294

Paired Samples Test for Moisture Contents

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Mimosa - H.abyssinica	1.00000	.22804	.09309	.76069	1.23931	10.742	5	.000
	Mimosa - A.nilotica	-.20000	.60332	.24631	-.83315	.43315	-.812	5	.454
	Mimosa - A.zanthophloea	-1.91667	1.04195	.42538	-3.01013	-.82320	-4.506	5	.006

Paired Samples Test for Total solubles

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Mimosa - H.abyssinica	7.39900E1	1.40684	.57434	72.51361	75.46639	128.826	5	.000
Mimosa - A.nilotica	6.33333E1	.99532	.40634	62.28881	64.37786	155.863	5	.000
Mimosa - A.zanthophloea	6.03000E1	.83427	.34059	59.42449	61.17551	177.047	5	.000

Paired Samples Test Soluble non-tannins

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Mimosa - H.abyssinica	2.37333E1	1.05008	.42869	22.63134	24.83532	55.362	5	.000
Mimosa - A.nilotica	1.81333E1	.71461	.29174	17.38340	18.88327	62.156	5	.000
Mimosa - A.zanthophloea	2.21333E1	1.19778	.48899	20.87634	23.39032	45.263	5	.000

Paired Samples Test for Tanning strength

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Mimosa - H.abyssinica	-.01167	.29308	.11965	-.31924	.29590	-.098	5	.926
Mimosa - A.nilotica	.59167	.06274	.02561	.52582	.65751	23.099	5	.000
Mimosa - A.zanthophloea	-1.27833	.62729	.25609	-1.93664	-.62003	-4.992	5	.004

Paired Samples Test for pH

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Mimosa - H.abyssinica	-.40200	.05675	.02538	-.47246	-.33154	-15.841	4	.000
Mimosa - A.nilotica	2.90000	.30542	.12469	2.57948	3.22052	23.258	5	.000
Mimosa - A.zanthophloea	-.07667	.44230	.18057	-.54083	.38750	-.425	5	.689

Paired Samples Test for shrinkage temperature

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Mimosa - H.abyssinica	3.00000	1.30384	.53229	1.63170	4.36830	5.636	5	.002
Mimosa - A.nilotica	.50000	.77460	.31623	-.31289	1.31289	1.581	5	.175
Mimosa - A.zanthophloea	-2.00000	1.00000	.40825	-3.04944	-.95056	-4.899	5	.004