VEGETABLE TANNING; PART 1. INTRODUCTION.[1]

The manufacture of leather dates back thousands of years to prehistoric times, and until relatively recently vegetable tanning predominated. Vegetable tanned leather is produced using tannins from vegetable sources. Historically, whole plants or parts of them - such as leaves, fruits (berries, seeds, nuts, etc.), bark, or the wood – were used to make leather. In the middle of the nineteenth century, concentrated tannin extracts (e.g. powders) started to become available, and were quickly adopted by the leather industry. Coincidentally, a new mineral tannin (based on chromium) was emerging at the same time, and ultimately replaced much of the traditional (vegetable) tanning.

Vegetable tannins are examples of the secondary metabolites of higher '*vascular'* plants; materials other than the primary metabolites required for the life of the plant. The main types of secondary metabolites are:

- phenols (e.g. tannins),
- terpenoids (e.g. oils),
- alkaloids (e.g. drugs like cocaine), and
- glucosinolates (e.g. pungent/spicy chemicals in the taste of mustard).

Tannins may constitute 5 to 10% of the dry mass of plants (up to 70% in certain parts) where they provide some protection against damage by animals and pests (Das, et al., 2020).

Based on their general chemical structure there are four types of vegetable tannins:

- hydrolysable,
- condensed,
- complex (somewhat hydrolysable and/or condensed), and
- phlorotannins (based on phloroglucinol)

Only the first two have - traditionally at least - been used extensively in leather manufacture. *'Hydrolysable'* (susceptible to chemical separation) tannins, consist of:

- a sugar molecule joined to multiple gallic acid molecules (i.e. the '*gallotannins'*), or
- one or more hexahydrodiphenoic acid molecules (i.e. the '*ellagitannins*').

'*Condensed*' (combination of two of more molecules) tannins, consist of one of a range of *polyphenols* (proanthocyanidins) linked with gallic acid (Falcao & Araujo, 2018).

Historically important sources of vegetable tannins (Falcao & Araujo, 2018).

Name		Source	Tannin type		
Scientific	**Common**		**Condensed**	**Hydrolysable**	
				Ellagitannin	**Gallotannin**
Acacia mearnsii	mimosa/wattle	bark	+		
Betula spp.	birch	bark	+		

[1] This '*Introduction'* is the first of a series of brief articles describing some basic aspects of vegetable tanning. Follow-up articles will concentrate on the history, science, technology, and current developments related to vegetable tanning. More detailed information on all topics (including theory and practice) will be provided during inputs to training planned for later in 2022.

Caesalpinia coriaria	divi-divi	pods			+
Castanea sativa	chestnut	wood		+	
Coriaria myrtifolia	redoul	leaves		unspecified	
Cotinus coggygria/Rhus cotinus	smoke tree	leaves			+
Larix	larch	bark	+		
Mirtus communis	myrtle	leaves		+	
Picea abies	Aleppo pine	bark	+		
Quercus aegilops	valonea oak, Turkish oak	acorns		+	
Quercus coccifera	*garouille*	root		unspecified	
Quercus infectoria	Aleppo oak	galls			+
Quercus ilex	holm oak	bark	+	unspecified	
Quercus spp. (*Q. ilex*, *Q. robur*, *Q. petraea* and *Q. pyrenaica*)	oak	bark	+	+	
		wood		+	
Quercus suber	cork oak	bark	+	+	
Rhus coriaria	sumac	leaves			+
Salix spp.	willow	bark	+		
Schinopsis balansae, *S. lorentzii*	quebracho	wood	+		
Terminalia chebula	myrobalan	fruit		unspecified	

Historically, the exploitation of particular types of vegetable tannins was related to the local prevalence of the tannin-containing plants. Later, increases in the demands of the tanning industry lead to searches for exotic sources. Hence, the use of tannins from mangrove trees (various species) for example.

All tannins function by combining with the structural protein of hides and skins – collagen – precipitating it into a more stable form called *'leather'*. Chemicals that might be vegetable tannins range in size (molecular weight) from 500 to 30,000 Da. But, molecules much larger than 3,000 Da become progressively less useful for the manufacture of leather because of their physical dimensions.

Item	**Mass (Da)[2]**	**Diameter (nm)**
Carbon (C) atom	12	0.2
Phenol (C_6H_6O)	94	0.8
Chrome oxide (Cr_2O_3)	152	0.9
Tannic acid ($C_{76}H_{52}O_{46}$)	1,701	1.8

The intricate network of triple helix collagen molecules (micro-fibrils, fibrils and fibres) presents a formidable barrier within the hide or skin of a live animal. Some of the preliminary stages in the manufacture of leather involve the '*opening up'* the collagen network (within the dermis) to facilitate access and reaction by processing chemicals. Chrome oxide (used in conventional mineral tanning) is a relatively small sized chemical, and more easily able to penetrate collagen. Vegetable tannins are very much larger and heavier chemicals, and not so easily able to penetrate collagen to accomplish the tanning reaction. The vegetable tanning process may require tannin equivalent to 15 to 40% of the dry weight of the hide - or skin - collagen (Falcao & Araujo, 2018).

Historically, to provide for the completion of the time-consuming tanning process with plant materials, vegetable tanned leathers could not be sold until they had been processed of at least a year. The introduction of tannin extracts and mechanical agitation allowed for quicker processing. Rather than duration of the tanning process, or even the content of tannin, a more common measure of the tanning process is the change in the shrinkage temperature (Ts). The Ts of raw cattle hides – specifically the collagen within the dermis - is about 65°C. During vegetable tanning the Ts increases to about 85°C, and in mineral (chrome) tanned leather the Ts may exceed 100°C.

Vegetable tanning has long been used to change raw materials (hides and skins) into leather; and ultimately leather products (e.g. footwear, garments and miscellaneous goods). But, even a simple introduction to vegetable tanning reveals the scope for complications associated with the material itself, including:

- source of the tannin (species of plant, location within the plant, season, etc.),
- extraction method (solvent, temperature, etc.), and
- chemistry of the tannin (condensed, hydrolysable, etc.).

[2] 1.7×10^{-27} kg

This is complicated further by the scope for blending tannins, and using them (in the tannery) in different ways. And the complications of the vegetable tanning, have to be considered along with other issues like:

- the extensive variability of the raw material (hides and skins), and
- the very large range of finished (leather) products that can be manufactured.

Vegetable tanning has persisted for thousands of years - developing by trial-and-error - and was only challenged by mineral tanning during the Industrial Revolution (1760 to 1840). Now, increasing concern about the impacts of some industrial processes (like chrome tanning) is prompting renewed attention to understanding more *'natural'* processes – like vegetable tanning – to identify more environmentally acceptable, and sustainable ways of manufacturing leather.

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