



Today's view on vegetable extracts in wet-end processing

Franck Diaz, Stahl

Vegetable tannins are compounds of vegetable origin from various parts of trees and plants. They have been known and used by tanners for over two thousand years, but until the 19th century they were mainly used in the form of raw, untreated material such as bark⁽¹⁾. Then chemical companies began to increase the tanning content yield by extraction using an autoclave followed by spray drying. This resulted in extracts such as chestnut or mimosa with more than 70% concentrated tanning power.

Even so, the main use of vegetable extracts lay in vegetable tanning or heavy vegetable retans. The famous East Indian tanning (IE tanning) process used myrobolam (*terminalia chebula*), avaram (*assia auriculata*), Konnam (*Cassia fistula*) extracts or a combination of myrobolam and mimosa (*acacia mearnsii*) extracts, mainly selected on the basis of high tan content⁽²⁾.

Increasing sales of automotive leather and the use and promotion of natural products, have led to more and more applications of vegetable derivatives in modern leather manufacturing processes.

Vegetable tans are now used to reduce or prevent the formation of CrVI, promote antioxydation properties, improve burnishability and glazing, fix cationic dyes and nitrogen resins, give fullness to wet-blue leather and much more.

Nowadays, the specific function of the vegetable tan content is the more important thing to select than just the tanning. Vegetable tanning materials are selected, purified and blended to produce the right natural chemical in line with the specifications for the leather on which it is to be used.

Raw material

The typical plants and the main parts used to source tannins are given as *Panel 1*.

Sourcing of the raw materials and chemical processing can modify these natural tanning agents, and a profile of a range of vegetable tanning sources, extracts and their applications is given as *Panel 2*.

Properties and classification of vegetable tannins

Vegetable tannins could be defined as polyphenols of various molecular weights. The optimum tanning effects occurs with molecular weights from 600 to 3000⁽³⁾. Below 600, virtually no tanning action takes place. Above 3000 the formation of insoluble polymer leads to poor diffusion of the polyphenol. Vegetable tannins can be classified into two main groups:

1. HYDROLYSABLE TANNINS

These are esters of gallic acid with carbohydrate (sugar) and various ratios of gallic acid linked to the glucose central molecule. Tara is mainly one glucose linked with three gallic residues and one or two di-gallic, to give an average molecular weight of 1000 – 1100. Sumac and Divi-divi also belong to this group. and the structure of Tara is shown in *Panel 3*.

Ellagitannins: Among hydrolysable tannins, ellagitannins have a very complicated structure based on ester of hexahydroxydiphenic acid. They are of higher molecular weight than the gallic derivatives. In practice, this kind of

Panel 1: Sources of Tannins

Barks	Woods	Fruits & pods	Leaves	Roots	Plant galls
Wattle (<i>Acacia</i> sp)	Quebracho (<i>Shinopsis</i> sp)	Myrobolam (<i>Terminalia chebula</i>)	Sumac (<i>Rhus</i> sp)	Canaigre (<i>Rumex hymenosephalus</i>)	Oak (<i>Quercus</i> sp)
Oak (<i>Quercus</i> sp)	Chestnut (<i>Castanea</i> sp)	Valonea (<i>Quercus aegilop</i>)	Gambier (<i>Uncaria gambier</i>)	Rhubarb (<i>Rheum rhabarbarum</i>)	Allepo (<i>Quercus infectoria</i>)
Eucalyptus (<i>Eucalyptus</i> sp)	Oak (<i>Quercus</i> sp)	Divi-divi (<i>Ceasalpinia coraria</i>)	Dhawa (<i>Anogeissus latifolia</i>)		Tamarix (<i>Tamarix articulata</i>)
Avaram (<i>Cassia auriculata</i>)	Cutch (<i>Acacia catechu</i>)	Algarobilla (<i>Ceasalpinia brevifolia</i>)			Pistacia (<i>Pistacia</i> sp)
Babul (<i>Acacia Arabica</i>)	Wandoo (<i>Eucalyptus wandoo</i>)	Tara (<i>Caesalpinia spinosa</i>)			Chinese (<i>Rhus semialata</i>)
Willow (<i>Salix caprea</i>)		Teripod (<i>Caesalpinia digyna</i>)			
Mangrove (<i>Rhizophora</i> sp)		Cashew husk (<i>Anacardium occidentale</i>)			

**Panel 2: Profile of a range of vegetable tanning sources and extracts and their applications**

Anacardium occidentale: This is an evergreen tree that grows to an average height of 20 metres. It is mainly cultivated for the collection of cashew nuts for the food industry and for the cashew nut shell liquid present in the fruit which is used in the varnish and paint industry.

Husk, the residue left after peeling the kernel, contains a fair percentage of tannin. The main advantages are the high percentage of antioxidants epicatechin and tocopherol which both act as free radical scavengers.

Husks are washed, dried, finely ground, sieved and blended with other useful ingredients into a proprietary formulation for adjusting pH and astringency. It is highly recommended for deep, lightfast dyes, for white leather with a vegetable character and for enhancing heat fastness on chrome free leather.

Caesalpinia spinosa: Known as Tara, this is a shrub or small tree up to five metres high that grows in the Interandean region, especially Peru.

The pods are the part of the tree selected for the purpose of tanning. They contain a high percentage of tannin (above 50%) from the hydrolysable family as well as gallic acid.

These components make the product ideal for chrome-free tanning with a good lightfastness. A most important parameter is the de-ironing process and the final particle size.

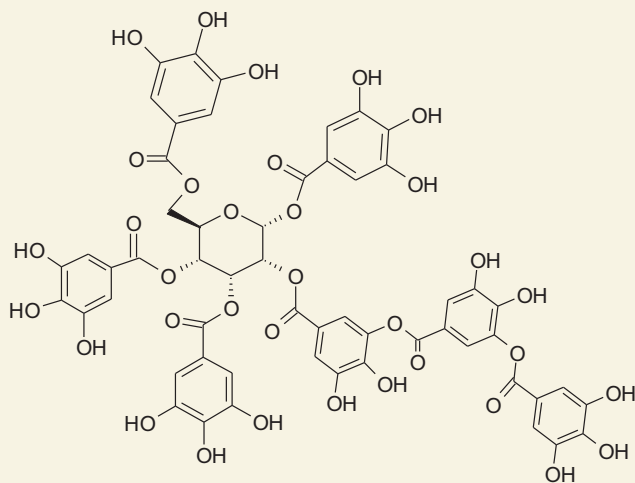
Rhus coriaria: Commonly known as "sumac," these are shrubs and small trees that can reach a height of 10 metres. This specific species is cultivated in the Mediterranean area.

The leaves contain a high percentage of gallotannin, a natural free radical scavenger like ascorbic and gallic acid. For tanning purposes, the leaves are collected, dried, finely ground and then sieved.

Sumac is prone to high iron and chlorophyll content but extracts can be chemically bleached, adjusted to right pH and made less sensitive to iron and with this treatment become an ideal product for use as a CrVI scavenger. It is also used within nubuck production, and is recognised for print retention.

Uncaria gambier: Gambia is a wild shrub which grows in Malaysia and Indonesia. Its leaves contain a high percentage of tannin, waxes and useful mineral. The leaves cannot be ground. Instead, extraction has to take place first. The extract is then dried as a cube and crushed into fine powder. The main tanning extract is low molecular weight polyphenol of catechin structure. Gambier can be bleached to remove the red tone. If it is not de-waxed, there is a strong reactivity while burnishing or glazing. This is an ideal compact product for use on shoe upper leathers.

Castanea sativa: Known as chestnut, this species within the broader Castanea Species grows in central and southern Europe, mainly France and Italy, and is used in the tanning industry. The tannin is extracted from the wood, sweetened and spray dried. The yield is fairly high, containing mainly vescalagin and castalagin derivatives.

Panel 3: Structure of Tara gallotannins

tannin gives firmer leather due to high binding capacity with the fibre. The product is acidic in nature and so has self-fixing properties. This was the main use in older times of oak extract in vegetable pits and chestnut, oak, myrobolam, and valonea all belong to this group. The structure of hexahydroxydiphenic acid is given in *Panel 4*.

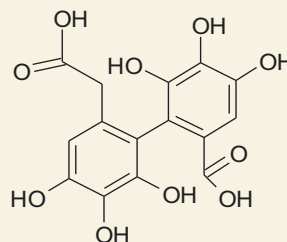
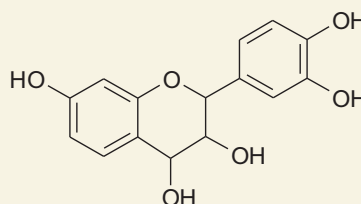
2. CONDENSED TANNINS

Condensed tannins do not hydrolyse but are prone to oxidation and polymerisation. As a result they are not lightfast but will bring high fullness to the leather due to their higher molecular weight.

The structure is based on combined flavonoid derivative such as the flavanne-3-ol or flavanne 3,4 diol with various degrees of condensation⁽⁴⁾, and this structure is shown in *Panel 5*.

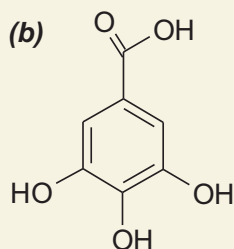
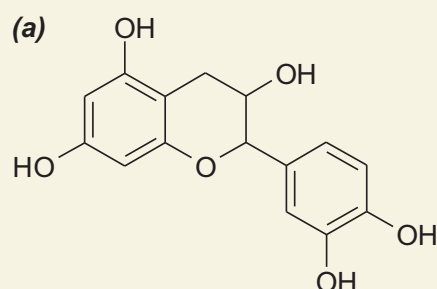
Catechic tannins: These are polymers of the above structures. Quebracho has more than 50% of its components above the pentamere from molecular weight 1000 to 15000. Gambier extract has lower polymerisation components and less tannin. This is compensated by the presence of natural wax and thickener which gives this particular product its properties of tightness, fullness and glazing ability.

Chemicals present in the vegetable tan having a molecular weight of less than 600 are sugar, organic acids such as gallic acid, pectin, lignin, antioxidant and gum. They are very important in the modern tanning and retanning formulations as they give specific performances to the product.

Panel 4: Structure of Hexahydroxydiphenic Acid**Panel 5: Structure of Flavanne 3,4 diol**



Panel 6: Structure of Epicatechin (a) and Gallic Acid (b)



Antioxidants: These are very useful as they prevent the leather from heat yellowing and, in the case of chrome tanning, from the formation of CrVI. All polyphenols have antioxidant properties but the activity has been shown⁽⁵⁾ to be higher with low molecular weight polyphenols. Products with a high percentage of gallic acid and epicatechin, like cashew husk, give an excellent whitening effect to leather. In addition, other components of this vegetable extract are organic acid derivatives and gum which can combine easily with the chrome and give full, white and lightfast leather. Leather retanned using this extract can be much whiter than tara retans. The dye colour is not affected and is very bright because of the mordant properties of the organic acid. Gallic acid is one of the best scavengers of CrVI, and tannins such as tara or sumac are highly recommended for this purpose as they naturally contain a fair percentage of this component. The structures of Epicatechin and Gallic acid are shown in *Panel 6*.

Polysaccharides: These give moisture balance to the final leather providing a better control of softness. Somehow, these sugars act as organic filler when the polymerisation rate is higher. Despite the low tanning power of cashew husk, this

kind of vegetable tan gives excellent properties to leather that are superior to classic commodity tanning extract.

Practical use and comparison

The components of vegetable extract all have an influence on the characteristics of the leather. Just as the nature of tan, hydrolysable or condensate is important, so the non-tan, antioxidant, acid, polysaccharide filler, gum and other non-tans are also important. The value of sourcing these natural raw products, extraction techniques and the way that any modifications are made need to be taken into close account. These factors need to be carefully managed and controlled to provide a consistent product. The base and attributes of a range of these products are set down as *Panel 7*.

Vegetable tanning extracts in tanning and retanning

Knowing the effect of the main chemicals present in vegetable extracts, tanners can combine these valuable products to achieve their target. As an example, cashew with its high content of antioxidant could be used alone, or combined with tara for chrome-free automotive leather. Tara will bring the tan content fairly lightfast to tan the leather

Panel 7: Properties and characteristics of some vegetable extracts

Vegetable Extract	Main bases	Colour on leather	Leather softness	Antioxidant activity	Grain retention	Tan content	Filling action	Grain tightness
Sumac (Legend 1)	Tannic acid gallic acid	Light green	+++	++	+++	++	+	+++
Tara (Legend 2)	Galloyl ester gallic acid	Off white	++	+	+	+++	+	++
Cashew (Legend 3)	Epicatechin Tocopherol	White	+	+++	++	+	+++	++
Gambia (Legend 4)	Epicatechin Wax, gum	Light brown	++	+	+	+++	++	+
Chestnut (Bleached) (Legend 5)	Ellagic acid vascalagin	Light brown	+	-	++	+++	+	+++
Chestnut (modified) (Legend 6)	Acrylic acid Ellagic acid	Light beige	++	-	+++	+	+++	+
			- hard + not soft ++ soft +++ very soft	- nil + fair ++ good +++ strong	- nil + fair ++ good +++ strong	+ 10-20 % ++ 20-30% +++ >30%	+ fair ++ good +++ strong	+ fair ++ good +++ strong



and cashew will improve the heat and lightfastness to a higher degree.

In the same kind of leather, the process could continue with vegetable tanning during retanning. Modified chestnut could be used to give roundness and print retention as a retanning compact system which would replace a syntan, acrylic and vegetable combination.

Some of the vegetable combinations are also very useful during the dyeing process. Sumac and cashew are excellent mordants for basic dyes. This means they combine easily with the cationic dyestuff, improving its fixation and avoiding bronzing, two common drawbacks of basic dyes. Cashew also enhances the deepness of acid dyes as it does not contain any sulphite. However, it does contain some strong antioxidants which stabilise the strength of the dyestuff.

With shoe upper leather, limited stretch, softness, tight grain and good reactivity to heat are basic parameters. Gambier extract has been proved to be well suited, and is widely used for the production of box-calf and glazed kid leather. Also, a combination of gambier with bleached chestnut could combine the advantages of gambier with the high tightness characteristics of the chestnut family in current shoe and bag leathers.

Specialised products can also be used to advantage with vegetable extracts to enhance and extend their natural properties. These products can be used to speed the penetration and prevent iron patches (*Legend 7*), provide better dispersion (*Legend 8*), and provide a whitening (*Legend 9*). ☺

Legend

Products by Stahl:

- (1) *Synektan SU*
- (2) *Synektan TP*
- (3) *Synektan VW*
- (4) *Synektan GA*
- (5) *Synektan CC: In this product the chestnut is double bleached and made less astringent than in crude extract. This allows fast and homogeneous penetration especially on wet-blue, making it ideal for vegetable-like leather and giving the specific spring of chestnut.*
- (6) *Synektan R-982: In this product the polyphenol is copolymerised with an acrylic monomer through a complex redox system, to produce a unique resin-like vegetable polymer. This gives full, rounded leather with fairly good tanning properties and good resistance to oxidation.*
- (7) *Bemanol SW:*
- (8) *Synektan NBN, LE:*
- (9) *Synektan PN*

References

- (1) *Edwin Aslam, Practical polyphenol, 1998*
- (2) *Dr Sundaran Rao, vegetable tanning material of India , Indian leather, Jan 2001*
- (3) *J C Beckley, Production of vegetable tanning extracts, 1988*
- (4) *Pure & Appl. Chem., Vol. 61, No. 3, pp. 357-360, 1989.*
- (5) *Xinguyan, Study on the removing and preventing CrVI in chrome leather, China Leather, 2008*