

# TANNINS, POLYPHENOLS - USES & BENEFITS

By R.O.B.Wijesekera

## What are Tannins and Polyphenols?

The use of vegetable material to process animal hides into leather, termed "Tanning", was indeed one of the world's oldest crafts. It had been used by mankind since the dawn of recorded history. However the mechanism of tanning of hides with vegetable extracts and their conversion to leather was only elucidated in modern times after the advent of sophisticated instrumentation. Tanning is now believed to be the crosslinking of the collagen chains of the animal skins, by the large molecules which are part of the vegetable tanning material. Tanning of leather is now conducted with mineral materials as well, as represented by alum tanning and chromium tanning. The natural plant material used for the tanning of animal hides is found globally within many different families of higher plants such as on the woods of the chestnut and oak, in *Divi-divi*, *Sumach*, *Myrobolans*, and plant galls.

It is recorded that the term "Tannin" was used for the first time in 1796 to indicate substances present in the vegetable extracts capable of forming insoluble complexes with the proteins of animal skins by preventing the action of the proteolytic enzymes that could affect the physical nature of the hides. This is the process that has been practiced over the millennia and has developed into a major industry namely, the leather industry.

The chemistry of these vegetable tanning materials varies widely. They are polyphenolic compounds mainly, that is compounds containing multiple phenolic groups, generally containing a high molar mass. High contents of these tanning material now referred to collectively as "Tannins" are found in nearly every part of the plant such as: barks, woods, leaves, fruits, roots, and even seeds. In biological terms it is presumed that an increased tannin formation can be associated with some sickness in the plant and the biological role of the tannins is believed to be as protection against infection, insect attack or animal herbivore. When extracted from the plant material and dried the tannins appear as brown solids, with an astringent taste.

In medieval times tannin containing plant material had been used for medicinal purposes, and as foods and beverages. In traditional medicine in China and Japan, and in Ayurvedic and Siddha medicine in the Asian region, tannin containing plant extracts were used to combat diarrhoeas, as diuretics, against stomach and duodenal tumours, as anti-inflammatory and

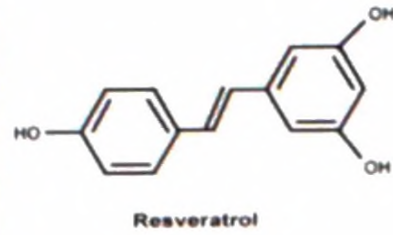
antiseptic agents, and as haemostatic agents. These are plants that contain what are now generally referred to as polyphenols.



*The tanning of leather*

Whereas all tannins are necessarily polyphenols, all polyphenols are not tannins, in respect of the fact that all polyphenols cannot be used to tan hides in the approved manner. These are the polyphenols derived from fruits and such sources that are used as foods and medicines which though polyphenolic are generally composed of smaller molecular weight compounds. Resveratrol which is a component of red wines and has acquired a reputation as a polyphenol with much health giving potential is one such.

Recent research also points to the role of tannins and polyphenols as the active agents in many efficacious traditional remedies; and the role of anti-oxidants are stressed in recent researches. Many types of tannins and polyphenols have displayed extensive biological activity such as anti-viral, anti-bacterial, and anti-tumour activity. It has also been shown that certain polyphenols can selectively inhibit HIV replication.



### Chemistry & Structural Classification of Tannins

The chemistry of Tannins is quite complex and experimentally forbidding. This was so when the great chemist and Nobel Laureate Emil Fisher did his classical work in Germany. The tradition was followed in Heidelberg by Freudenberg followed by Otto Theodore Schmidt who with the new tools of instrumental analyses was able to unravel the complexities.

Modern research has enabled the chemical structural diversity of the tannins to be explored. Early classifications identified two categories, but currently four main categories are recognised as:

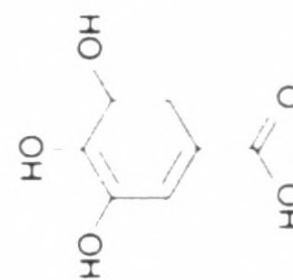
1. Gallotannins
2. Ellagitannins
3. Complex tannins
4. Condensed Tannins.

Gallotannins (1), are those tannins in which galloyl units (units of gallic acid groups), are bound to diverse polyol-, catechin, or triterpenoid units. When hydrolysed they give rise to Gallic acid.

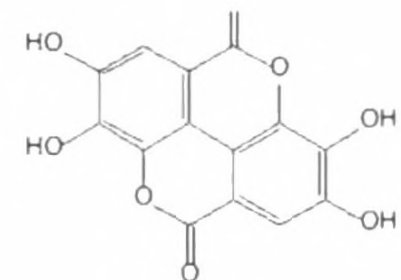
Ellagitannins, (2), are those in which at least two galloyl units are C-C coupled to each other and do not contain a catechin unit, linked with a sugar unit. When hydrolysed they yield mainly ellagic acid and gallic acid.

Complex tannins,(3), are tannins in which a catechin unit is bound to a gallotannin or ellagitannin unit with a sugar unit.

Condensed Tannins, (4), are all oligomeric and polymeric pro-anthocyanidins, formed by linkage of a C4 of one catechin with a C-8 or C-6 of the next monomeric catechin.



*Gallic acid*



*Ellagic acid*

Condensed Tannins are those that are not hydrolysable with such ease and are in chemical nomenclature, oligomeric and polymeric pro-anthocyanidins, based on the anthocyanidin scaffolding. They are also termed pro-anthocyanidins, which means they are a group of polyhydroxyflavan-3-ol oligomers and polymers linked by C-C bonds between flavonol sub-units.

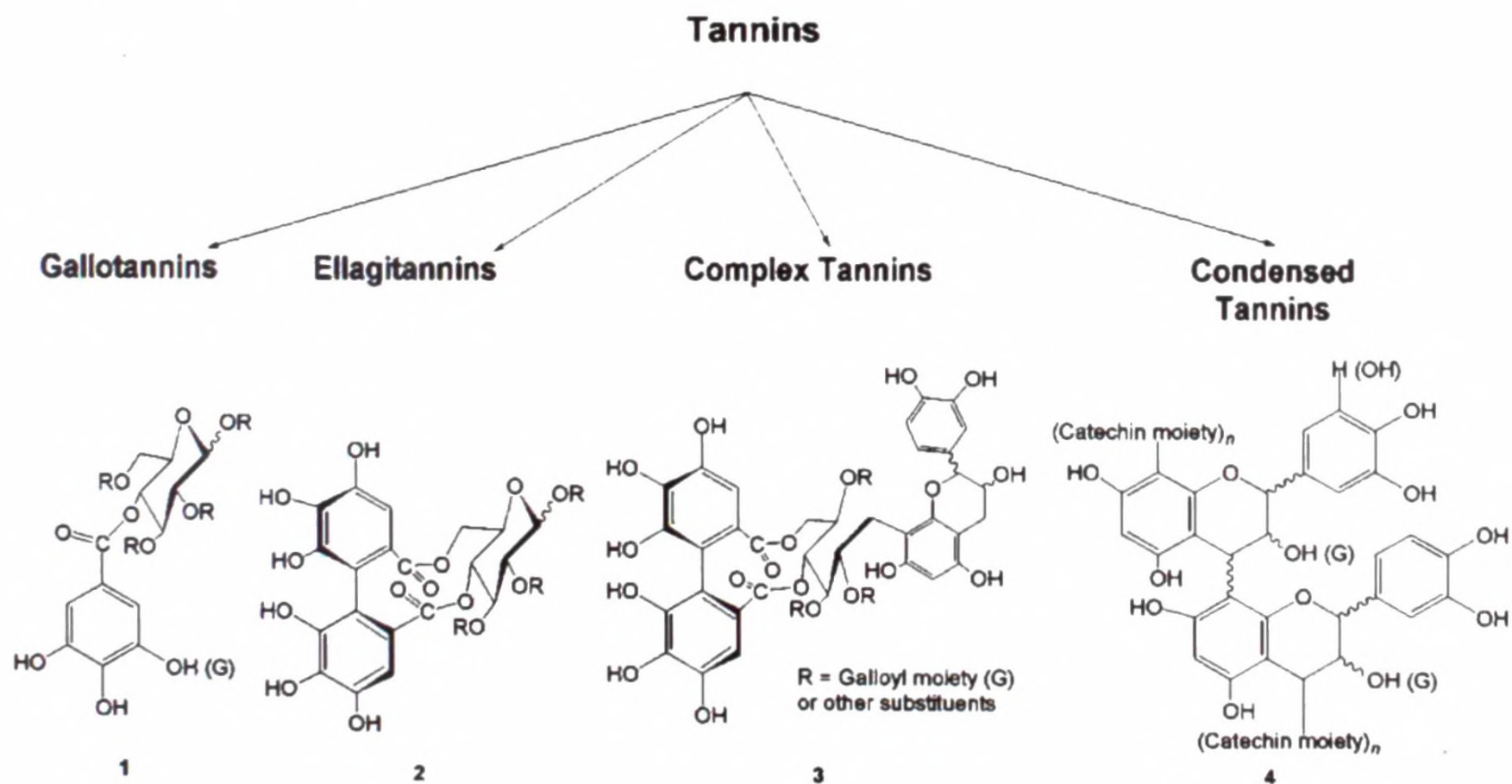
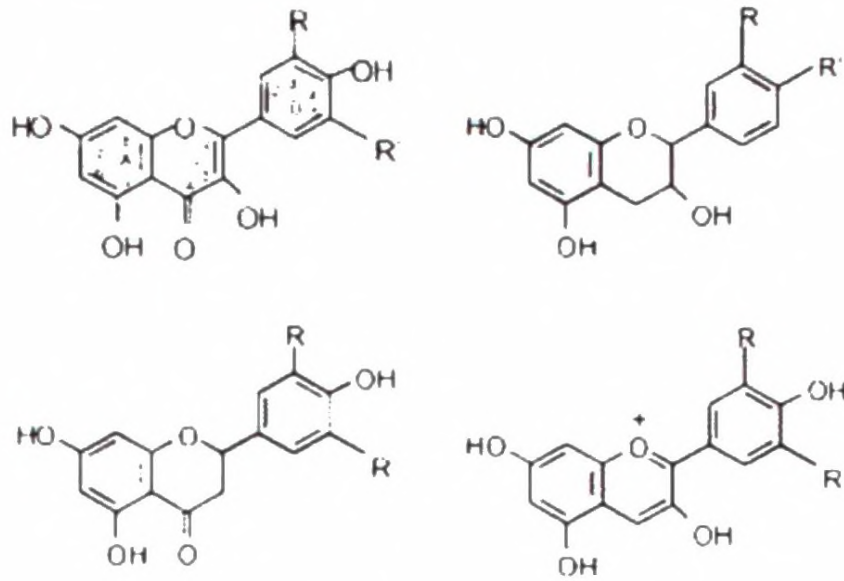


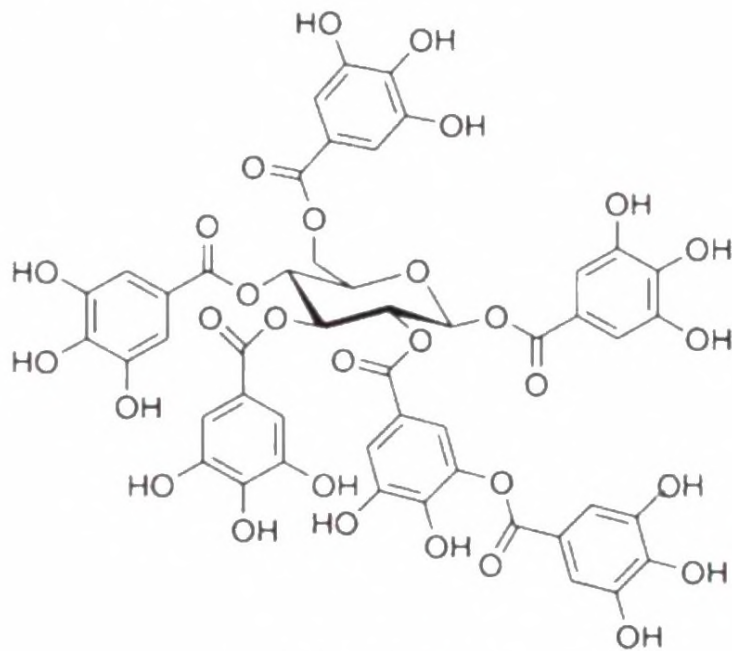
Fig. 1: Classification of the tannins.

Accordingly they are referred to as Flavonoids, and flavonoid derivatives.



Typical flavonoid structures

The Gallotannins and Ellagitannins are sometimes referred to as Hydrolysable Tannins, since they are readily hydrolysed by acids or enzymes to yield ellagic and gallic acids. A central sugar unit with galloyl groups or ellagic acid groups attached to the carbon atoms of a sugar molecule are their characteristic structural feature.

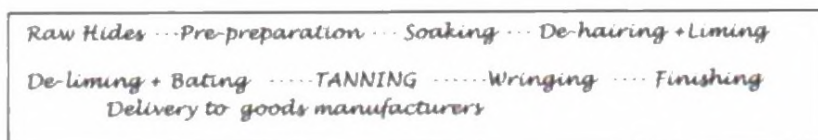


Hydrolysable Tannin

### The Leather Tanning Process

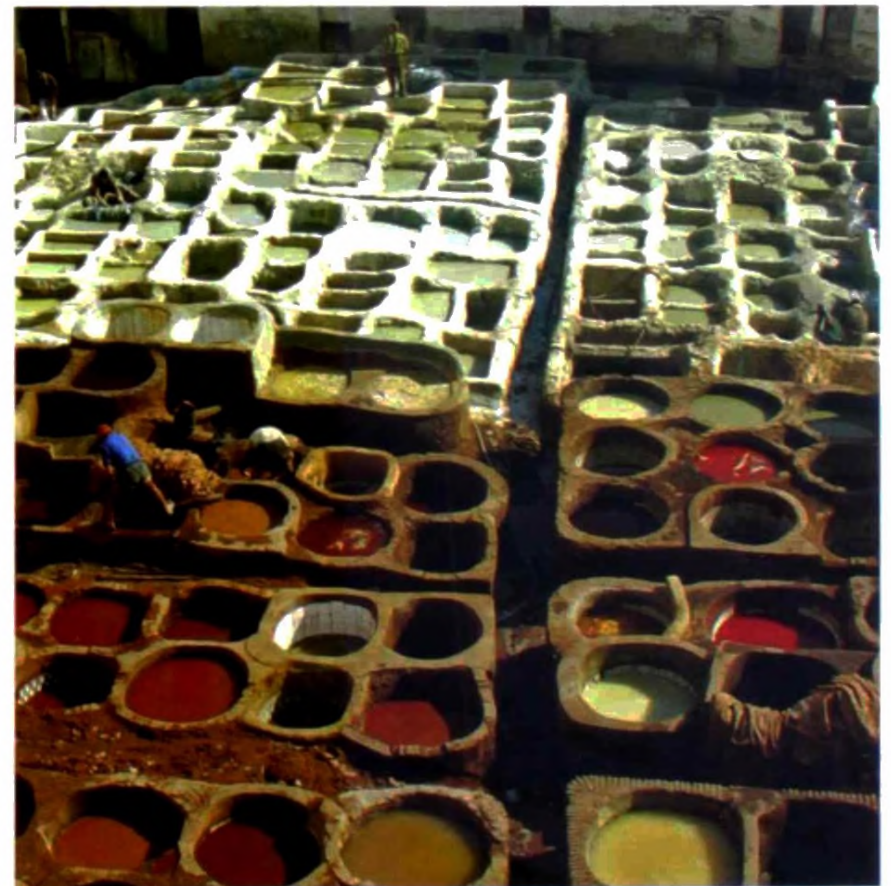
It is interesting and pertinent in the context to understand the essentials of the process for the tanning of hides to produce commercial leather.

The process flow for tanning of hides for the production of leather is represented as follows:



Raw Hides-----Soaking-----Liming + De-hairing----- de-liming + Bating-

The main goal of the process of tanning is to convert the raw animal hides, which are perishable, to the desired stable product which is leather. In modern times the majority of the leathers produced, with the exception of speciality leathers, are tanned with chromium salts. However in ancient times the major tanning material was indeed of vegetable origin. Here we shall discuss the tanning process, with vegetable tannins. Vegetable tanning is believed to be the most classic, traditional and in cases of certain types of leather the most preferable method although it is agreed that environmental pollution is at a maximum with this methodology. It was even during ancient times considered a trade that generated considerable malodours. Accordingly tanneries were even in the earliest times located in areas far from the cities and dwelling places. Cities such as Lyon and Grasse in France now famous in their own right were originally regarded as evil smelling places on account of a tanning industry located there. Attention to the unpleasant odoriferous exudates of the industry form one of the major factors in modern times as eco-friendly methods have necessarily to be employed to avoid atmospheric pollution. Trades that in modern times employ vegetable tannin to produce leather, argue that the texture and characteristic odour of the leather produced by this technique is "natural". They also state that such leathers are produced by skilled craftsmen blending the best natural vegetable extracts with selected natural oils, and fat liquors. The smell of leather it is claimed then becomes a perfume for leather lovers. Handbags, briefcases, portmanteaus, wallets, rugs, belts, chairs, seats, boots and saddles, are some items where the preference for tanning the leather has been vegetable tannins; and add to this the smell of new leather in luxury models of cars.



Vegetable extracts in a Tannery



Preparation of the hide

In the modern tanning process skilled craftsman use vegetable tannins which are commercially available both in liquid and powder form. The most popular extract is that obtained from the chestnut wood, and it is the classical and most valued tanning material. Equally popular is the tannin obtained from the Argentinian tree, known as *Quebracho* Tannin. This extract is known as one that gives the leather a special reddish tint and a characteristically warm feel and a bright appearance. Another extract, namely *Tara* Tannins are the ones used to produce leathers for the automobile industry for use as upholstery material. They are deemed to maintain appearance under hardwearing conditions. Mimosa extracts, also called *tanwat* give a rose colour to the hides, and are used to obtain leathers for shoe uppers and soles. Gambier extracts are mainly used for full grain and fine articles, and *myrobalan* tannins produce leathers with a uniform colour and softness of feel. So there is variety in the tanning process employing vegetable tannins, and the craftsmen are able to use the diverse extracts to produce leathers for a multiplicity of different uses.

The following are the various stages in the complex process of the tanning of leather (with special reference to the tanning with the use of natural vegetable extracts).

#### Stages in tanning.

##### Pre-preparation:

Raw hides from the slaughter houses are preserved for transportation to the tanneries by a process of "Pickling and

drying". This is to arrest deterioration by enzyme action, which would cause rotting and generation of malodours.

#### Operations at the Tannery.

- **Soaking.**

The dry preserved raw hides are enabled to regain their normal content of moisture by soaking in water. Soaking is preceded by removal of dirt and contaminants, salt and residual matter.

- **Removal of Hairs, - Liming.**

Removal of hairs and extraneous flesh is carried out in a medium of lime and sulphide.

- **Deliming, - Bating**

The hides are then neutralised (deliming), with ammonium salts and weak acid pressed, to flush out any impurities together with the excess water. The hides then becomes flaccid. It is then treated with proteolytic enzymes, - enzymes similar to those in the digestive system to clean the grain and make the pelt smooth and silky.

This removes hair roots or roots of the wool, and pigments.

- **Vegetable Tanning Process**

The hides are transferred to vats in which they are hung in series. A rocker arrangement enables the liquor in the vats to be agitated.

The hides are next transferred to a second series of lay-away vats without agitation. In these vats progressively increasing concentrations of tannin liquor are used. Vegetable tannins are polyphenolic compounds of two broad types. Hydrolysable Tannins are those like Chestnut and Myrobalans, and condensed tannins as exemplified by wattle and hemlock. The mechanism behind the process of vegetable tanning is the formation of hydrogen bonds between the phenolic groups of the tanning material, with the peptides of the protein chains in the hide. It has been recorded that even as much as 50% of the tannin material can be incorporated into the hide in the tanning process.

- **Wringing**

The excess moisture after tanning is removed by wringing between rollers.

#### Finishing Operations

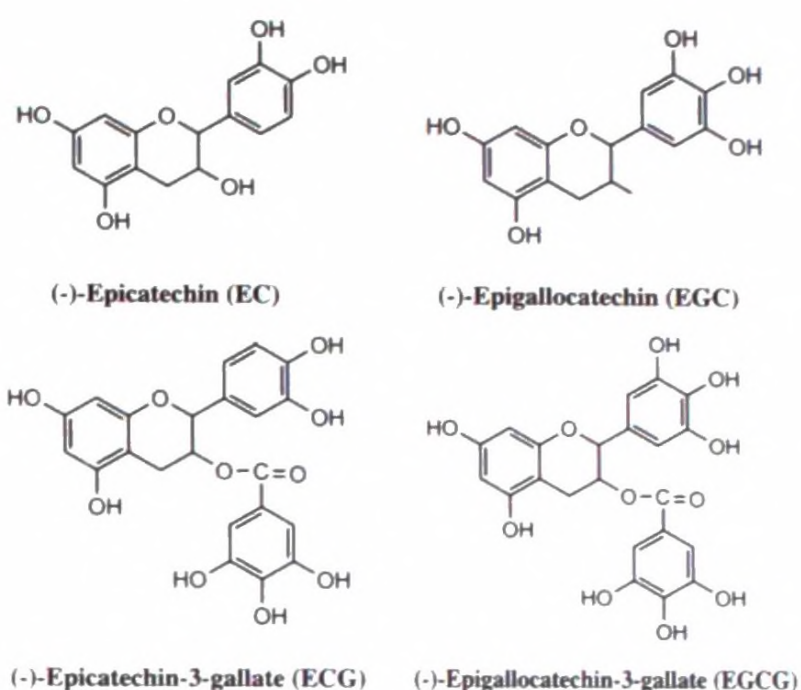
The finishing operations are chemical and mechanical and are

designed according to the nature of usage of the crude leather. Various oils, pigments, mechanical toning, pressing methods are used to get the final finish of the leather before it can be sent to the product manufacturers.

In the modern tanning process, vegetable tannins processed and available in both liquid and powdered forms are used. From the wood of the chestnut tree the most famous and ancient tannin extract is obtained. Almost equally popular in vegetable tanning is the *Quebracho* extract obtained from the wood of a tree that grows primarily in Argentina. This extract gives the leather a special reddish tint with an unmistakable warm touch and bright appearance. Mimosa extracts which are reputed to give the hides a special rose pink hue are deemed suitable for leather in shoe uppers, and soles. Gambier extracts are used for full grain and fine valuable articles, while the extracts from *Myrobalans* are said to produce leathers with a uniform colour and soft touch. *Tara* tannins are mainly used to produce leathers for automotive upholstery, where durability resilience and strength are important.

### Some Health Benefits of Tannins & Polyphenols

Tannins and polyphenols from plant sources represent a wide variety of chemical structures. All of them bear the characteristic of possessing many phenolic groups attached to large molecular scaffoldings. That is why the collective term "Polyphenols" is used to refer to them. Many of the tannins used in the tanning process are those that have very large molecular weights, though a few of them have lesser molecular weights. Tea polyphenols and their health benefits have been known to mankind for many years. Modern research has definitely demonstrated the specific benefits of tea tannins, although there are the sceptics who are unable to explain these and so wallow in disbelief. The characteristic polyphenols of tea, *Camelia sinensis*, are the "Catechins" represented as four main types. The displayed benefits are known to fall into the categories in the figure.



### Health Benefits of TEA The Polyphenols of Green Tea

The chemical nature of the main tea polyphenols are as depicted above. They are different to the polyphenols in the extracts that are generally used for the tanning of leathers. The health benefits of tea are such that Ayurvedic specialists tend to classify it as a *Rasayana*, mostly because of the effect on degenerative diseases. Research on the effects of dietary polyphenols on human health conducted during the past decade strongly supports a role for them in the prevention of degenerative diseases, particularly cardiovascular diseases and cancers. The anti-oxidant properties of the polyphenols have been intensely studied, and it is clear that their action extends beyond the modulation of oxidative stress. The main dietary sources are: fruits, plant derived beverages, such as tea, red wines, vegetables cereals and legumes. Recent studies on animal models indicate effective results of polyphenols as anti-amoebic agents, antibacterial agents, antifungal agents and even anti-viral agents. For example extracts of *Terminalia chebula*, - a plant widely used in the Ayurvedic pharmacopoeia and a main constituent of the Ayurvedic preparation known as *Triphala*-, showed significant protective effects when applied to the epithelial cells infected with the influenza A virus in vitro. Extracts have shown anti-herpes simplex virus type 1 activity and significant inhibitory activity on the effects of human immunodeficiency virus 1 reverse transcriptase.

A methanol extract of *T. chebula* was studied for the effects on the growth of malignant cell lines including a human (MCF7) and a human osteosarcoma cell line (HOS 1), a human prostate cancer cell line (PNT 1A). The extract was found to decrease cell viability, inhibit cell proliferation, and induce cell death in a dose dependent manner. A tannin fraction from *T. chebula* was also reported to have anti-mutagenic activity in vitro, and in another study a high potential for inhibiting the growth of leukaemia cells was observed.

A variety of other potential clinical benefits have indeed been observed which underscores the value of the tannin containing plants as more than promising multi-drug candidates yet to be fully developed. The results underscore the benefit of following leads from the uses in traditional pharmacopoeias which trail is being followed avidly by modern researchers.

#### Reference Sources

1. Haslam E. (1989). Plant Polyphenols. Cambridge University Press. Cambridge.
2. Hagerman, A.E. (1992). Tannin Protein interactions. In Ho, Lee, Huang, eds., Phenolic Compounds in Food and their Effects on Health. 1. Analysis, Occurrence & Chemistry. ACS. Washington DC. Chap. 19, pp 236-247.
3. Heidemann, E. (1993). Fundamentals of Leather Manufacture. Eduard Roether. KG.
4. Sahunkhe, D.K., Chavan, I.K., & Kadam, S.S., (1989), Dietary Tannins: Consequences and Remedies. CRC Press. Boca Raton, Florida.
5. Scalbert, A., Johnson, I.T., & Saltmarsh, M. (2005). Polyphenols, Anti-oxidants and Beyond. Amer. J. Clin. Nutr., 81(1), 2155-75.
6. <http://www.drugs.com/npp/terminalia.html?printable=1>
7. Anwesa, B., Bhattacharya S.K., & Chatopadhyay, R.R., (2013). The Development of Terminalia chebula Retz. In Clinical Research, Asian Pac. J. Trop. Biomed. 3(3), 244-252.
8. Khanbabaee, K., & van Ree, T., (2001). Tannins: Classification and Definition. Nat. Prod. Reps. 18, 641-649.
9. Chung, K-T., Wong, T.Y., Wei, C., Huang, Y-I., & Lin, Y., (1998). Tannins and Human Health: A Review, Crit. Revs. Food Sci. & Nutr. 38(6), 421-464.
10. <http://www.toddcaldecott.com/index.php/herbs/361-haritak>

#### De-mining operations

De-mining operations are essentially a post conflict requirement and is hazardous, costly, and time consuming. Despite sophisticated new technology that is currently available, many explosive devices are still cleared manually with the help of trained animals. For example, a rat can check the ground faster than a man with a metal detector. Dozens of giant pouched rats tethered by deminers are used to sniff out landmines.

*Economist Technology Quarterly 7th June 2014.*

#### Primitive menus - Could eating like our ancestors make us healthier?

The Tsimane a primitive tribe in the Amazon of lowland Bolivia enjoy porridge of plantains and sweet manioc. They get most of their food from the river, the forest, or fields and gardens carved out of the forest.

However, a diet that revolves around meat and the dairy will take a greater toll on the world's resources than one based on unrefined grains, nuts, fruits, and vegetables.

The popularity of so-called Stone Age diets is based on the idea that modern humans evolved to eat the way hunter-gatherers did during the Palaeolithic period.

The Bajau of Malaysia indulges in fishing and diving for everything they eat. Some live in houses on the beach or on stilts; others have no homes besides their boats.

The Kyrgyz of the Pamir Mountains in northern Afghanistan live at a high altitude where no crops grow. Survival depends on the animals that they milk butcher and barter.

The real hallmark of being human therefore is not our taste for meat but our ability to adapt to many habitats and to craft many healthy diets,

Adapted from: Ann Gibbons: in The Evolution of Diet, *National Geographic*, Sept. (2014)

#### Food problems

When we think of threats to the environment, we tend to picture cars and smokestacks, not dinner. But the truth is, our need for food poses one of the biggest dangers to the planet. Agriculture is among the greatest contributors to global warming, emitting more greenhouse gases than all our cars, trucks, trains, and aeroplanes combined, - largely from methane released by cattle, and rice farms, nitrous oxide from fertilised fields, and carbon di oxide from the cutting of rain forests to grow crops or raise livestock.

National Geographic .vol, 225, No,5,(2014)