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Review Article

Plants and secondary metabolites (Tannins): A Review

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Abstract: The objective of this review was to investigate and identification of structure and role of the tannins in plants. During growth and maturation period in plants, some substances can be found in structure of them which they have essential role in plant fortune. These substances are called plants secondary metabolites. One of the most important of secondary metabolites is Tannins. The function of tannins in plants is a much discussed by previous researchers issue. A great deal of research with tannins has followed an approach that looks at biological relationships: taxonomy, phylogeny, biosynthesis, nutritional and physiological effects on herbivorous animals e.g. ruminants. Tannins are defined as phenolic compounds of high molecular weight ranging from 500 to more than 3000 which they found in plants leaves, bark, wood and bound to proteins that form insoluble or soluble tannin-protein complexes. They have been closely associated with plant defense mechanisms towards mammalian herbivores and insect. Tannins are divided into two main groups, according to their chemical structure and properties: hydrolysable (HT) and condensed tannins (CT). Hydrolysable tannins are usually found in lower concentrations in plants than CTs. Condensed tannins consist of flavanoid units (flavan-3-ol) linked by carbon-carbon bonds. They are found in many plant species such as Acacia *spp*, *Sericea lespedeza* as well as pasture species such as *Lotus spp*. In recent years many researchers demonstrated that tannins have positive effects on animals by anti microbial, anthelmintic, protein bypassed effects in ruminants.

Keywords: plants secondary metabolites, Tannins, Hydrolysable tannins, Condensed tannins.

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Introduction

Plants secondary metabolites

For million years, humankind is completely dependent on plants as source of carbohydrates, proteins and fats for food and shelter. In addition, plants are a valuable source of a wide range of secondary metabolites, which are used as pharmaceuticals, agrochemicals, flavours, fragrances, colours, biopesticides and food additives. The number of known chemical structures is estimated to be nearly fourfold greater than that in the microbial kingdom. The United State market sales of plant medicinals have risen up about US$ 3 billion per year (Ramachandra Rao and Ravishankar, 2002).

During growth and maturation period in plants some substances can be found in structure of them which they have essential role in plant fortune. These substances called plants secondary metabolites (Hagerman and Buther, 1981; Hassanpour *et al,* 2011). It has been suggested that accumulation of secondary compounds in plants is dependent upon photosynthetic capacity, season, rain and temperature (Mooney *et al,* 1975).

Groups of natural plants secondary metabolites of higher plants are shown in table 1. One of the most important secondary metabolites is polyphenols (e.g. tannins) (Hagerman and Buther, 1981; ChaichiSemsari *et al,* 2011; Hassanpour *et al,* 2011; Maheri-sis *et al,* 2011). A great deal of research with tannins has followed an approach that looks at biological relationships: taxonomy, phylogeny, biosynthesis, etc.

Polyphenols are the most widely distributed class of plant secondary metabolites and several thousand different compounds have been identified. Polyphenols play many different roles in plant biology and human life, including UV protective agents, defensive compounds against herbivores and pathogens, contributors to plant colors, contributors to the taste of food and drink, and pharmaceuticals (Haslam,, 1989; Hassanpour *et al,* 2011).

Table 1. Groups of natural secondary metabolites of higher plants

Phenylpropanoids	Alkaloids	Terpenoids	Quinones	Steroids
1. Anthocyanins	1. Acridines	1. Carotenes	1. Anthroquinones	1. Cardiac glycosides
2. Coumarins	2. Betalaines	2. Monoterpenes	2. Benzoquinones	2. Pregnenolone derivatives
3. Flavonoids	3. Quinolizidines	3. Sesquiterpenes	3. Naphthoquinones	
4. Hydroxycinnamoyl derivatives	4. Furonoqui nones	4. Diterpenes		
5. Isoflavonoids	5. Harringtonines	5. Triterpenes		
6. Lignans	6. Isoquinolines			
7. Phenolenones	7. Indoles			
8. Proanthocyanidins	8. Purines			
9. Stilbenes	9. Pyridines			
10. Tannins	10. Tropane alkaloids			

Adapted from Ramachandra Rao and Ravishankar, 2002.

What is Tannin?

Tannins are defined as phenolic compounds of high molecular weight ranging from 500 Da to more than 3000 Da which they found in plants leaves, bark, fruit, wood and roots located basically in the tissues in the vacuoles. They have been closely associated with plant defense mechanisms against mammalian herbivores, birds and insects (Hagerman and Buther, 1981; Hassanpour *et al,* 2011). Except of some higher molecular weight structures tannins are soluble in water (20- 35°C). Oligomeric compounds with multiple structure units with free phenolic groups can complex with proteins, starch, cellulose and minerals. In the plant kingdom tannins are found in both flowering plants and non-flowering plants. They are found in many plant species such as Acacia *spp*, *Sericea lespedeza* as well as pasture species such as *Lotus spp*. (Hassanpour *et al,* 2011).

Tanniniferous plants are widespread in nature and although a lot of attention has been given to their study in recent years, the term "tannin" continues to be difficult to define accurately. Indeed, whereas related phenolic compounds such as simple phenolics, neolignans and flavonoids are characterised and classified according to their chemical structure, tannins are a diverse group of compounds that are related primarily in their ability to complex with proteins (Fahey and Jung, 1989; Hassanpour *et al,* 2011). Thus, tannins are usually defined as water-soluble polyphenolic substances and have ability bound to proteins that form insoluble or soluble tannin-protein complexes. As a consequence, tannins able to make complex with polysaccharides (cellulose, hemicelluloses and pectin) and nucleic acids, steroids, alkaloids, and saponins (Haslam, 1986; ChaichiSemsari *et al,* 2011; Maheri-sis *et al,* 2011). There are some observations with regard to the presence of tannins that deserve some attention. For example, within plant cells, tannins are found in the vacuole (Chafe and Durzan, 1973; Lees *et al,* 1995) and this has been suggested to be a method to preventing inhibition of the cell metabolism by tannins (Haslam, 1974). Also, one must astound about the energetic costs and on the reasons for such a practice, especially when plants devote so much carbon to the production of tannins. Haslam (1986) was suggested secondary metabolism serves to maintain primary metabolism in circumstances not propitious for growth. In recent years many researchers demonstrated that tannins have positive effects on animals by anti microbial, anthelmintic, protein bypassed effects in ruminants (Athanasiadou *et al,* 2001; ChaichiSemsari *et al,* 2011; Hassanpour *et al,* 2011; Maheri-sis *et al,* 2011; Sadaghian *et al,* 2011).

Types of Tannin

According to their chemical structure and properties, tannins are divided into two main groups: hydrolysable (HT) and condensed tannins (CT) (Athanasiadou *et al,* 2001; ChaichiSemsari *et al,* 2011; Hassanpour *et al,* 2011; Maheri-Sis *et al,* 2011). The characteristics of the two groups are different in molecular weight, structure and produce a different effect on the herbivorous animals especially on ruminant when ingested. According to the chemical structure (Fig 1) of HTs (gallotannins and ellagitannins) are molecules which contain a carbohydrate, generally D-glucose, as a central core (Min and Hart, 2003). The hydrolysable groups of these carbohydrates are esterified with phenolic groups, such as ellagic acid or gallic acid (Mangan, 1988; Haslem, 1989). Hydrolysable tannins are usually found in lower concentrations in plants than CTs. Hydrolysable tannins are subdivided into taragallotannins (gallic and quinic acid) and caffetannins (caffeic and quinic acid) (Mangan, 1988). They are hydrolyzed by tanninase enzymes which engage in ester bond hydrolysis. HTs can form compounds such as pyrogallol which is toxic to ruminants. Toxic compounds from more than 20% HT in the diet can cause liver necrosis, kidney damage with proximal tuberal necrosis, lesions associated with hemorrhagic gastroenteritis and high mortality, which were observed in sheep and cattle (Reed, 1995). Hydrolysable tannins can also affect monogastrics by reducing growth rates, protein utilization and causing damage to the mucosa of the digestive tract and increasing the excretion of protein and amino acids.

Condensed tannins (CT or proanthocyanidins), are the most common type of tannins found in forage legumes, trees and stems (Barry and McNabb, 1999). These types of tannins are widely distributed in legume pasture species such as *Lotus corniculatus* and in several kinds of acacia and other plant species (Degen *et al.,* 1995). Condensed tannins have a variety of chemical structures affecting their physical and biological properties (Min *et al.,* 2003). They are consist of flavanoid units (flavan-3-ol) linked by carbon-carbon bonds. The complexity of CT depends on the flavanoid units which vary among constituents and within sites for interflavan bond formation. The term proanthocyanidins (PAs) is derived from the acid-catalyzed oxidation reaction producing red anthocyanidins upon heating PAs in acidic alcohol solutions. Anthocyanidin pigment is responsible for the colors observed in flowers, leaves, fruits juices and wines. The astringent taste of some leaves, fruits and wines is due to the presence of tannin.

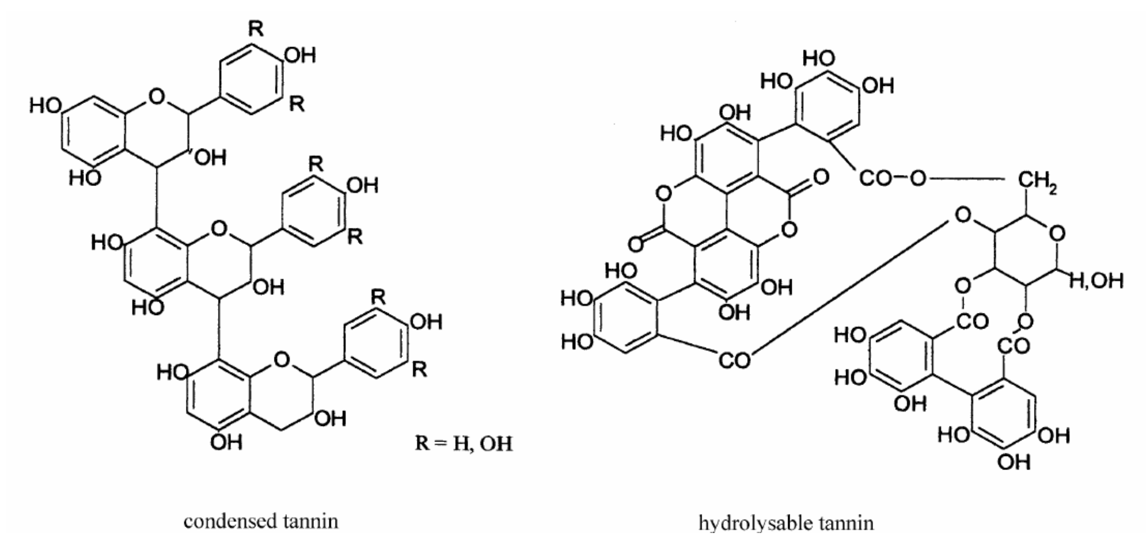

Figure 1. Chemical structure of CTs and HTs. Adapted from McSweeney *et al* (2001).

Condensed tannin biosynthesis

Biosynthesis of tannins is shown in fig 2. According to Gottlieb (1990) which provided a clear and concise summary of plant metabolism when he stated: “The basic metabolism of autotrophic plants combines photosynthesis with respiration, leading from CO_2 via the sugars of the Calvin cycle, Pyruvic acid and acetic acid either to the fatty acids of the Lynen spiral (a reversible process) or to the simple aliphatic acids of the Krebs cycle and thence back to CO_2. Connected by mostly reversible pathways are some essential intermediates such as the Krebs-cycle-derived aliphatic amino acids, the purines and the pyrimidines, the acetic acid-derived Mevalonic acid, the sugar-derived glycerol and the sugar-plus pyruvic acid-derived Shikimic acid, the latter functioning as a precursor to the aromatic amino acids.” Indeed, the shikimic acid and acetate-malonate pathways are the major metabolic routes of polyphenolic synthesis in plants. Also, two precursors are necessary for flavonoid synthesis, acetate and phenylalanine (Van Soest, 1982; Jung and Fahey, 1983).

Additionally, Stafford (1990) observed for the synthesis of CTs, a flavan-3, 4,-diol is one of the immediate precursors and the other is usually a flavan-3-ol acting as a nucleophile. In tracer studies with a range of fruit-bearing plants using a variety of labelled cinnamate precursors, this author showed that the C6-C3 carbon skeleton of the cinnamate precursor was incorporated intact into the flavan units. Many factors can affect CTs biosynthesis in plants. Foo *et al* (1982) suggested that because polymers isolated from the leaves and roots of the same plant show structural variation, biosynthesis of tannins may be under different control in the two tissues. They reported two independent processes of tannin biosynthesis in mutants of *L. pedunculatus*: (a) light mediated and occurring in the apical meristem, and (b) nutritional and occurring in the root system. Biosynthesis of CTs in leaves was controlled by light quality and in the roots by stressing the plants by applying conditions of nitrogen deficiency. Condensed tannin concentration in plant tissue has been shown to vary with many factors. These include plant species (Jackson *et al,* 1996), plant part (Foo *et al,* 1982, Barahona *et al,* 1997), plant maturity (Lees *et al,* 1995), growing season (Feeny, 1970) and soil fertility (Barry and Forss, 1983; Barry, 1989).

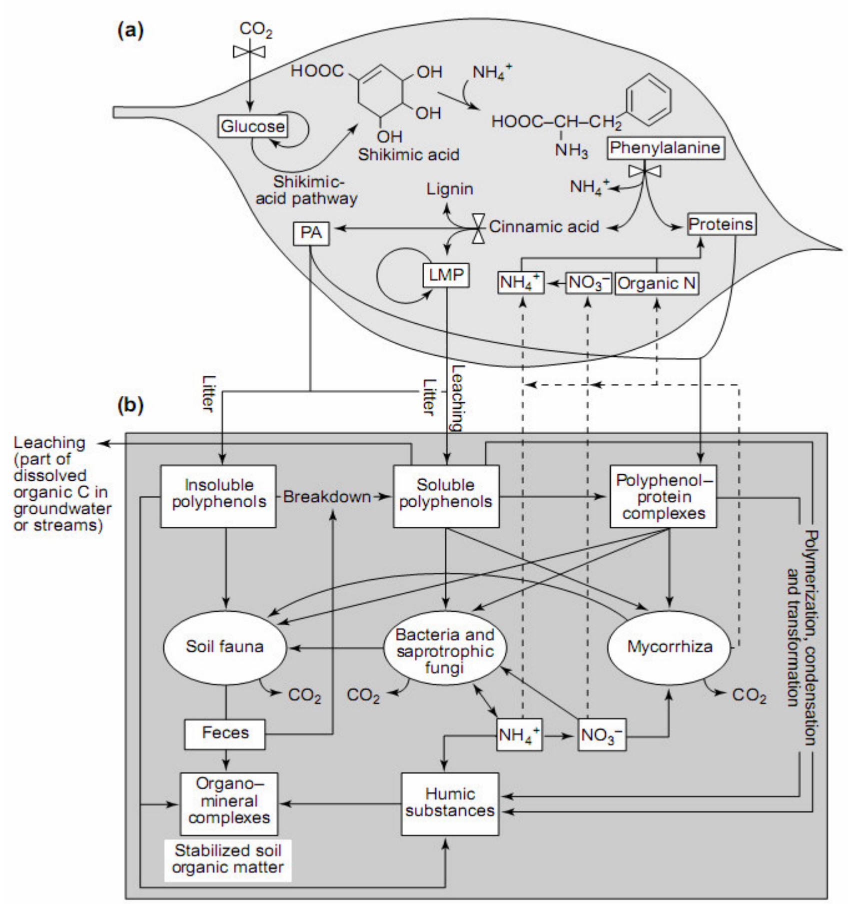

Figure 2. Biosynthesis of tannins, Adapted from Hättenschwiler and Vitousek (2000). The diagram shows a simplified overview of biosynthesis [(a) represents any living plant tissues], release into the environment and fate of polyphenols in the soil (b). The unbroken lines indicate the biosynthetic pathways of polyphenols, and their fluxes and transformations into and within the soil. The broken lines indicate nitrogen (N) uptake by the plant. The aromatic amino acid phenylalanine, synthesized in the shikimic-acid pathway, is the common precursor of proteins and phenolic compounds. Low molecular weight phenolics (LMP) might undergo a high turnover in living plant tissues, whereas high molecular weight PAs are considered to be metabolic endproducts with minimal turnover and a tendency to accumulate with the aging of plant tissues. Major control mechanisms (indicated by the regulation symbol ►◄) occur at the level of the availability of glucose and phenylalanine (mainly quantity of polyphenols), and at the level of cinnamic acid (polyphenol quality). Soil organisms influence not only the uptake and metabolism of phenolic compounds, but also the fragmentation, mixing and translocation of polyphenol-containing litter material (soil fauna), and the production of extracellular enzymes (microorganisms) that drive either the breakdown of insoluble polyphenols or the formation of humic substances from low molecular weight polyphenols (according to the polyphenol theory of humus synthesis). The uptake, transformation and/or metabolism of polyphenol–protein complexes by soil organisms might be a major link between polyphenols and nutrient cycling (Hättenschwiler and Vitousek, 2000).

Benefits of Tannins

In the tropics, the efficiency of forage-based ruminant production systems is limited by forage quality and forage quantity during the dry season (NAS, 1979). In most tropical regions, native grasses from permanent pastures constitute the most important feed resource for ruminants. Unfertilised and unmanaged native grasses generally have poor nutritive value: 2.5-7.0 % crude protein (dry matter basis) and low dry matter digestibility 40-50 % (Patraa and Saxena, 2010). During the dry season, which ranges from two to six months, the dry matter availability from these pastures diminishes dramatically. Furthermore, the low levels of crude protein and minerals in tropical grasses tend to decline rapidly during the dry season. As a result, cattle lose weight and milk production drops (NAS, 1979; Patraa and Saxena, 2010). During the wet season, the protein level in most grasses is lower than the level necessary for adequate animal growth (Patraa and Saxena, 2010). In addition, the low digestibility of tropical grasses can limit animal production, being on average 13 % less digestible than temperate grasses (Minson and McLeod, 1970). Although not yet fully exploited, the strategy of incorporating forage legumes into feeding schemes such as cut and carry systems or protein banks has enormous potential towards solving the severe nutritional limitations that ruminants face within tropical production systems (Devendra, 1990). Indeed, improved animal performance has been frequently reported in response to the use of high quality tanniniferous forages as supplements for ruminants fed low-quality roughage diets. Additionally (Gonzalo Hervás *et al,* 2003) was demonstrate that moderate amounts of CTs have been reported to exert beneficial effects on protein metabolism in ruminants, decreasing rumen degradation of dietary protein and increasing absorption of amino acids in the small intestine. Hence, The CT may enable dietary protein bypass from the rumen for digestion in the lower digestive tract (Hassanpour *et al,* 2011). An increase in flow of metabolizable protein or essential amino acids to the small intestine has been observed in animals grazing forages of high CT content compared to those grazing a low CT diet (Waghorn, 2008).

Tannin sources

In deed, tannins can be found in nearly all of the legumes, shrubs, vegetables and fruits in the world. For example sorghum (Reed, 1995), tea, wine (Corder *et al,* 2006) and pomegranate (Scalbert *et al,* 2003). Also, Previous researchers observed that high levels of CT have found in *Acacia species (e.g. saligna, mearnsii, decurren, dealbata, pyonantha)* (Athanasiadou *et al,* 2001; Waghorn, 2008; Max, 2010; Hassanpour *et al,* 2011; Sadaghian *et al,* 2011), red wood (*Quebracho tannins*) (Athanasiadou *et al,* 2001; Waghorn, 2008; ChaichiSemsari *et al,* 2011; Maheri-sis et al, 2011), birdsfoot trefoil (*Lotus corniculatus*), sainfoin, (*Onobrychis*), sulla (*Hedysarum coronarium*) and lotus major (*L. pedunculatus*) (Waghorn, 2008).

Conclusions

During growth and maturation period in plants some substances can be found in structure of them which they have essential role in plant fortune. These substances called plants secondary metabolites. Tannins are defined as phenolic compounds and plants secondary metabolites which have beneficial effects on protein metabolism in ruminants, decreasing rumen degradation of dietary protein and increasing absorption of amino acids in the small intestine.

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