Chemical Composition of Some Commercial Tannins Produced in Turkey

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Abstract

This study was aimed to investigate the chemical composition of commercial tannins produced in Turkey mostly used by leatherworking. Tannin samples from pine bark, valonia, and gall nuts as well as ground sumac leaves were provided from the plant. It is well known that valonia, gall nuts, and sumac tannins compose of hydrolysable tannin whereas pine bark tannin consists of condensed tannins. Therefore methods of hydrolyzed and condensed tannins were applied in commercial samples. The methanol-water solubility of tannin samples was determined, after that total phenol content was assayed by spectrometrically in aqueous phase and ether phase. Amount of condensed tannin in the samples was determined by spectroscopical acid-butanol methods as well as stiasny number method gravimetrically. Content of gallotannin in samples was determined with Rhodanine Method; amount of ellagtannins was assayed with Nitrous Acid method. Functional group analysis of the tannin samples were investigated by FTIR instrument after compressing KBr pellets.

***Keywords*:** Tannin, Pine bark, Valonia, Turkish galls, Sumac, FTIR

Introduction

Tannin is commonly used in the leather industry as tanning material since the past. During tanning, these compounds that interact with proteins in animal skin for precipitate protein in the skin to provide make stabilized against the effect of bacterial degradation and gives flexibility. Also traditionally they are used for the needs of the local people as herbal drug. Furthermore tannins have been used as raw materials in medicine and pharmacology due to their antiviral, antimicrobial and anticancer effects. In addition, these compounds have used to clarify wine and beer, chemical and paint industry. Polyphenols are the most important secondary biomass in the non-wood forest products. However, nowadays, natural and renewable biomass sources especially in the chemical industry are more important with the increasing use and popularity. Many studies were aimed to use of plant tannins as natural phenolic compounds more area and efficient rather than petroleum-derived raw materials especially after the 1970s oil crisis in the world. Tannins were produced in commercially as preparation of low formaldehyde emission adhesives, ink production, dyeing of textile products and corrosion inhibitor (Bisanda, 2003)

Chemical structure of tannins are consist multiple adjacent polyhydroxyphenyl groups. This structure of tannins gives opportunity to bond with macromolecular compounds such as proteins, metal ions and polysaccharides (especially glucose) (Ozacar et. al., 2006).

There are two main groups based on constituent of tannins, these are hydrolysable and condensed tannins. Hydrolysable tannins are esters of formed by glucose with gallic acid and ellagic acid. It is easy soluble in water. Condensed tannins (proanthocyanidins) are polymers formed by condensation of flavanoid units. Main component of the condensed tannin is catechin and anthocyanindin. Although the tannins are natural condensed compounds, they are still having capable of condensation reaction with various chemicals as formaldehyde. Rigid carbon-carbon bond of condensed tannin possess cannot cleavage by hydrolysis (Bisanda et al., 2003).

According to Pizzi (2006) 200.000 tones of commercial tannins are produced worldwide each year and condensed tannins constitute more than 90% of the total world production. Species, trade names, and origin of commercial tannins of produced in the world are given in Table 1.

Table 1. Commercial Tannins in the World

Scientific Name	Trade Name	Origin	References
Schinopsis balance	Quebracho Tannin	Argentine	Mosiewicki et al.,(2004)
Acacia mearnsii	Mimosa Tannin	South Africa	
Acacia mearnsii	Mimosa Tannin	Brazil	
Acacia sp.	Mimosa Tannin	Italy	Zhao et al., (2010)
Quercus sp.	---	Tanzania	Bisanda et al., (2003)
Acacia sp.	Wattle Tannin	Chili	
Eucalyptus sp.	---	Brazil	
Salix caprea	Willow		
Acacia sp.	Wattle Tannin	Tanzania	Ndazi et al., (2006)
Acacia mangium	Mimosa Tannin	Malaysia	Hoong et al.,(2010)
Carya illinoensis	Pecan Nut Tannin		
Tsuga heterophylla	Hemlock bark extract	North America Canada	Franklin, (1980)
Castanea sativa	Chesnutt extract	Italy	http://en.silvateam.com/
Schinopsis balansae	Quebracho	South America	
Schinopsis lorentzii	Tannin	Argentine Paraguay	
Caesalpinia spinosa	Tara Tannin	Peru South America Northern Africa	
Uncaria gambir	Gambier extract	China, India Malaysia, Indonesia	
Terminalia chebula	Myrobalan extracts	East Indies	
Rhizophara sp.	Mangrove tannin	Nigeria	Sowunmi et al.,(1996)
Rhus sp.	Sumac extracts	Southern Europe	Pizzi., (2006)
Pinus sp.	Pine bark extract		
Vitis vinifera	Grape seed tannin	France	Ping et al., (2011)

The aim of this research was to investigate chemical composition with emphasis to phenolic compounds of pine bark tannin, valonia tannin, Turkish gall tannin, and sumac leaf from industrially produced in Turkey.

Materials and Methods

The tannin samples used in this study were supplied from Balaban Valeks Inc., Manisa, Turkey.

Determination of Phenolics

Methanol:water extraction of wood samples was performed as described previously (Balaban and Ucar, 2001). The Stiasny number reaction was used to determine the polyphenol content of extracts according to Yazaki and Hillis (1977). Total phenol content was determined by the Folin–Ciocalteu method (Singleton and Rossi, 1965). Gallotannins were hydrolysed with 1 M sulphuric acid, and gallic acid was then assayed using the Rhodanin reagent according to the method of Inoue and Hagerman (1988).

Gallic acid was used as the standard and assays were carried out in triplicate. The amount of ellagic tannin was determined with acidic sodium nitrite method by spectroscopically (Bate-Smith, 1972). The determination of proanthocyanidin was carried out as described by Govindarajan and Mathew (1965) and the results were expressed as cyanidin equivalents per amount of extracted wood (ε = 43.700; Fuleki and Francis, 1968).

FTIR Spectroscopy

Spectroscopic measurements were performed in a Bio-Rad Excalibur series FTS 3000 spectrophotometer using the standard KBr method (300 mg KBr plus 1 mg tannin; resolution: 4 cm^{-1}; 64 scans). The spectra were base line corrected at 3,700, 1,850 and 700 cm^{-1} and normalized to the highest band at 1,510 cm^{-1}.

Results and Discussions

Table 2 shows that the methanol-water solubility and total phenol content of commercial tannins. Pine tannin has high methanol-water solubility than other samples. Total phenol content of samples was determined ether and aqueous phases. Results of aqueous phase were similar while Turkish gall tannin had the highest value of ether phase.

Table 2. Methanol-Water Solubilities and Total Phenol Content of Commercial Tannins

Sample	Methanol-Water Solubility (%)	Total Phenol Content (mg g^{-1})	
		Ether Phase	Aqueous Phase
Pine Tannin	94.71	44.01	100.53
Valonia Tannin	82.93	26.60	104.45
Turkish Gall Tannin	67.61	53.72	102.44
Sumac Leaves	44.27	52.97	100.96

The stiasny number, proanthocyanidins, and pH in samples can be seen in Table 3. According to the results, pine tannin contains condensed tannins while other tannin samples contain hydrolysable tannins. Ozdemir (2010) reported the proanthocyanidin content for quebracho and mimosa tannins, respectively, 119.26 and 103.25. As can be seen from fourth column of the table, pH of pine tannin solution was higher. Valonia, Turkish gall tannin, and Sumac leaves had lower pH values due to hydrolysable tannins including gallic and ellagic acid.

Table 3.Condensed Tannin Amount and pH of Commercial Tannins

Sample	Stiasny Number	Proanthocyanidins (mg g^{-1})	pH
Pine Tannin	70.77	148.55	4.76
Valonia Tannin	nd.	2.03	3.81
Turkish Gall Tannin	nd.	nd.	4.24
Sumac Leaves	nd.	nd.	4.62

Sumac leaves include only gallotannin while valonia and Turkish gall tannin contain both of hydrolysable tannins, it was indicated in Table 4. Pizzi et al. (2009) had similar results for commercial hydrolysable tannins. It was stated that sumac leaves and Turkish gall tannin were occurred by mainly polygallic oligomers.

Table 4. Hydrolyzable Tannin Content

Sample	Hydrolyzable Tannins (mg g^{-1})	
	Gallotannin	Ellagic Tannin
Pine Tannin	15.12	nd.
Valonia Tannin	50.77	75.35
Turkish Gall Tannin	26.35	21.95
Sumac Leaves	30.79	nd.

The wide peak in the region 3550–3100 cm^{-1} is characteristic of the OH stretching vibration of benzene nucleus and methylol group of tannin (Ping et al. 2012; Ooa et al. 2009; Jianzhong et al. 2009; Puica et al. 2006; Kim and Joongkim, 2003; Ozacar et al. 2006). Small peak around 2900 cm^{-1} are due to aromatic CH stretching vibration of both methyl and methylene groups (Ping et al. 2012; Kim and Joongkim, 2003; Ozacar et al. 2006). The peaks pronounced at 1619-1450 cm^{-1} shows presence of aromatic rings (Ping et al. 2012; Ooa et al. 2009; Puica et al. 2006; Kim and Joongkim, 2003, Laghi et al. 2010, Ozacar et al. 2006). The region of peaks 1500-950 cm^{-1} are called fingerprint region for FTIR spectra of tannins.

The peak at 1285 cm^{-1} in the spectrum of pine tannin is a characteristic feature for the flavonoid based tannins (Edelmann et al. 2002). It was determined that the peak only for the pine tannin spectra (see Fig 1). According to Laghi (2010), oak tannins have characterized by bands at1324 and 1037 cm^{-1} due to symmetrical and asymmetrical C–O valence vibration. There is a peak at 1324 cm^{-1} in spectra's of valonia, Turkish gall, and sumac leaves. The carboxyl-carbonyl group appears at 1732 cm^{-1} in the spectrum of valonia tannin according to Ozacar (2006). The peaks around 910-740 cm^{-1} in all spectra's are deformation vibrations of the C-H bond in the benzene rings (Ping et al. 2012; Kim and Joongkim, 2003; Ozacar et al. 2006, Ozacar et al. 2008).

Figure 1. FTIR Spectra of Pine Tannin

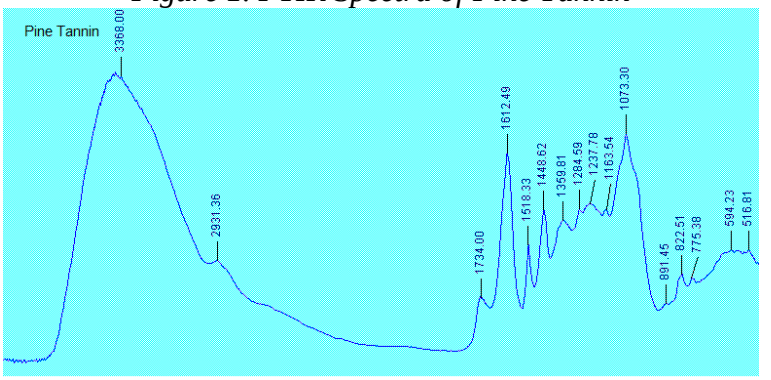


Figure 2. FTIR Spectra of Valonia Tannin

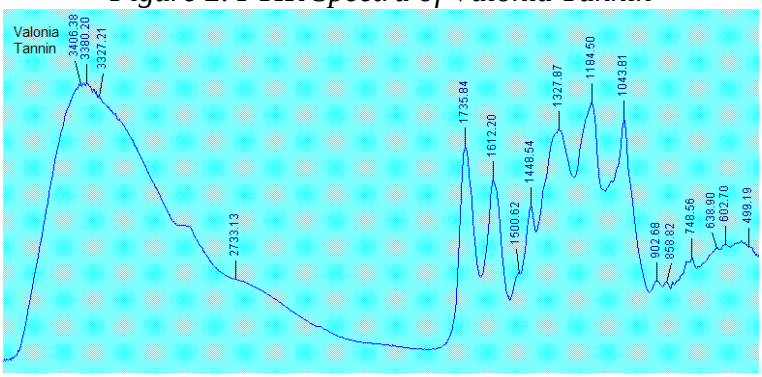


Figure 3. FTIR Spectra of Turkish Gall Tannin

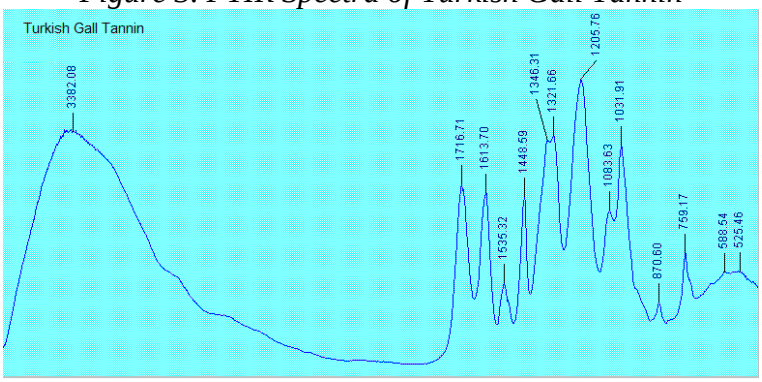
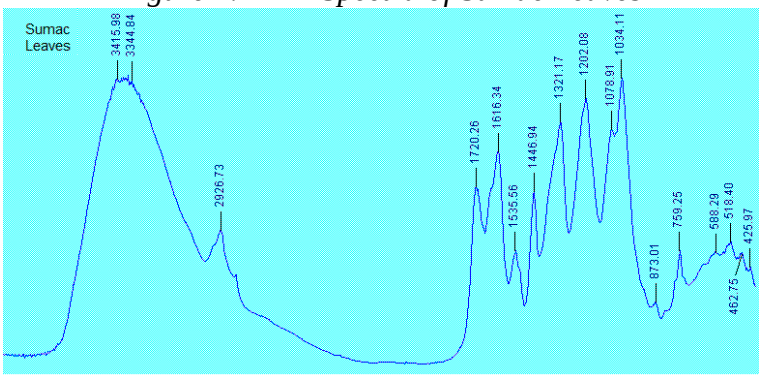


Figure 4. FTIR Spectra of Sumac Leaves



Conclusions

The results obtained in this study indicated that proanthocyanidisns is main constituent of pine tannins while gallo tannins for sumac leaves, gallo, and ellagic tannins for valonia and Turkish gall tannin. Based on the stiasny number analysis, pine tannins can be used in synthesis of tannin based bio-adhesives. The different functional groups were identified by FTIR investigation in this present study.

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