SHORT COMMUNICATION

Thermal properties of tannin extracted from *Anacardium occidentale L.* using TGA and FT-IR spectroscopy

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The chemical nature of the polyphenols of cashew kernel testa has been determined. Testa contains tannins, which present large molecular complexity and has an ancient use as tanning agents. The use of tannins extracted from cashew testa, considered in many places as a waste, grants an extra value to the cashew. In this work we have analysed through high performance liquid chromatography, infrared spectroscopy (FT-IR) and thermo gravimetric analysis the average molecular weight, main functional groups and thermal properties of tannins extracted from *Anacardium occidentale L.* The results of these analyses are compared with the commercial grade tannic acid. The FT-IR spectra showed bands characteristic of C=O, C–C and OH bonds. This important bioactive compound present in the cashew nut kernel testa was suggested as an interesting economical source of antioxidants for use in the food and nutraceutical industry.

Keywords: *Anacardium occidentale L.;* cashew testa; FT-IR; HPLC; tannic acid; TGA

1. Introduction

India is the largest producer and processor of cashews (*Anacardium occidentale L.*) in the world. Total area in India under cashew cultivation is about 868,000 ha with annual production of 665,000 tons, giving average productivity of 860 kg per hectare. India processed about 1,138,000 tons of raw cashew nut seeds through 3650 cashew processing mills scattered in many states of the country (Mohod et al. 2011). Cashew nut kernels are regarded as a nutritious food product, worldwide. The kernels of cashew nuts are externally covered with a thin and reddish-brown-coloured skin, known as testa. The testa constitutes about 1–3% of the total weight of cashew nuts and is found to provide a rich source of hydrolysable tannins with polymeric
proanthocyanidins as major polyphenols (Mathew & Parpia 1970). The outer skin of the cashew kernel contains about 25% of tannin material and 11% of non-tannin material, which has properties similar to that of imported wattle bark tannin used in the leather industry (Singh et al. 2006). Tannic acid, which has an estimated chemical formula $C_{76}H_{52}O_{46}$, is a commercial form of tannins. Three thousand years ago, Egyptians extracted these compounds and used them as tanning agents. Due to their tanning capacity, these compounds were very important at an industrial level and tanneries, although nowadays salts and synthetic tannins have acquired more importance against tannins extracted from natural sources (Matamala et al. 2000). Tannins are also used in dyeing, photography, refining beer and wine as well as an astringent in medicines (Nonaka et al. 1981). The antioxidant properties of tannins have awoken special interest in the corrosion area, since these compounds can inhibit corrosion in metals when they are incorporated in coatings. Many studies about corrosion inhibition using tannic acid or tannins extracted from pine, mimosa and acacia species can be found in the literature (Jaén et al. 2003; Hernes & Hedges 2004). Considering the great importance of this industrial waste and the potentiality for development of new eco-friendly compounds, the thermal stability of the tannins extracted from cashew testa was analysed by high performance liquid chromatography (HPLC), infrared spectroscopy (FT-IR) and thermo gravimetric analysis (TGA).

2. Results and discussion

Tannins were extracted from cashew testa samples. The molecular weights (MWs) obtained through HPLC for tannins from *A. occidentale* L and standard tannic acid were 2.240 and 2.322, respectively (shown in Supplementary Figure S1). The use of the HPLC procedure for the analysis of tannins offers the optimum approach since the compounds can be identified both qualitatively and quantitatively by the retention times (a unique characteristic of tannins under specified standard conditions) (Popov et al. 2003).

Figure 1(a) and (b) shows the spectrum of tannins and tannic acid where it can find a strong absorption around 3332.99 and 3334.92 cm$^{-1}$ with a wide and strong band positioning at 3268.99, 3217.27 and 3282.84, 3213.41, respectively. These bands are assigned to the hydroxyl groups (OH) stretching vibrations and due to the wide variety of hydrogen bonding between OH. The spectrum shows that the sharp peak at 2854.65 cm$^{-1}$ and a small shoulder at 2694.56 cm$^{-1}$ are associated with the symmetric and antisymmetric $\text{–C–H–}$ stretching vibrations of CH$_2$ groups, respectively. The deformation vibration of the carbon–carbon bonds in the phenolic groups absorbs in the region of 1500–1400 cm$^{-1}$. The spectrum of tannins compared with tannic acid.

Figure 1. (a) and (b): Infrared spectroscopy of tannin and tannic acid (standard).
acid and tannins showed a decrease in many peaks which are not strong as is observed in tannic acid. Also, the other report observed that only the tannic acid contains some aromatic esters due to the signal characteristics bands of carbonyl groups: C=O stretching vibration at 1730–1705 cm\(^{-1}\) and C–O at 1100–1300 cm\(^{-1}\) (Stuart \textit{2005}; Silverstein & Webster \textit{2006}) and positioning at 3268.99, 3217.27 and 3282.84, 3213.41, respectively. These bands are assigned to the OH groups stretching vibrations and due to the wide variety of hydrogen bonding between OH. The spectrum shows that the sharp peak at 2854.65 cm\(^{-1}\) and a small shoulder at 2694.56 cm\(^{-1}\) are associated with the symmetric and antisymmetric \(\text{C–H–}\) stretching vibrations of CH\(_2\) groups, respectively. The deformation vibration of the carbon–carbon bonds in the phenolic groups absorbs in the region of 1500–1400 cm\(^{-1}\). The spectrum of tannins compared with tannic acid and tannins showed a decrease in many peaks which are not strong as is observed in tannic acid. Also the other report observed that only the tannic acid contains some aromatic esters due to the signal characteristics bands of carbonyl groups: C=O stretching vibration at 1730–1705 cm\(^{-1}\) and C–O at 1100–1300 cm\(^{-1}\) (Stuart \textit{2005}; Silverstein & Webster \textit{2006}). Detailed information is listed in Table S1; these results are similar to those reported in the literature for polyphenolic compounds as tannic acid (Socrates \textit{2004}).

TGA is a thermal analysis technique used to quantify mass changes in a material as a function of heat. The TGA traces and mass spectra obtained for the tannins and tannic acid heated at a rate of 5°C cm\(^{-1}\) are shown in Figures 2 and 3, which showed the dependence of the mass loss of the samples expressed as percentage of the initial mass and temperature.

Figure 3 shows the tannin samples from cashew testa had an initial weight of 4.86 mg (sample weight). When heat was applied, the percentage of mass loss between the temperature of 29.47°C and the complete dissociation temperature at 60°C was 89.91%, and 5%, respectively. After that, the mass was found to be in the steady state condition (main degradation was observed in this range). Finally, after 500°C, no change in the mass loss was observed.

TGA of tannic acid in Figure 3 shows three thermal zones, the first one is appreciated between 30.9 and 180°C with a mass loss at 93.35%. In the second level, degradation was done at
the temperature between 200 and 210°C and a mass loss of 88.53% and the complete degradation was observed at 380–600°C, while in cashew gum, decomposition temperature was around 240°C (Mothé & de Freitas 2014).

3. Conclusion
The study of the cashew industry waste cashew testa (A. occidentale L) has revealed its importance as valuable material for the tannin industry. HPLC, FT-IR and TGA analyses provided the MW, functional characteristics and thermal stability. TGA analysis showed similar thermal stability properties for both tannins and tannic acid, which also have more depolymerisation stages due to the easy break in smaller structures than tannins. Hence, this study observed that cashew testa, an industrial waste containing tannins, is a unique candidate for the production of gallic acid which can be used for cancer studies.

Supplementary material
Experimental details relating to this paper are available online at http://dx.doi.org/10.1080/14786419.2015.1040992.

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Disclosure statement
There is no conflict of interest.

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