



Analysis of commercial proanthocyanidins. Part 1: The chemical composition of quebracho (*Schinopsis lorentzii* and *Schinopsis balansae*) heartwood extract

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ARTICLE INFO

Article history:

Received 4 April 2011

Received in revised form 23 June 2011

Available online 5 November 2011

Keywords:

Schinopsis lorentzii and *Schinopsis balansae*

Anacardiaceae

Quebracho

Electrospray mass spectrometry

Proanthocyanidins

Natural polymer

ABSTRACT

Quebracho (*Schinopsis lorentzii* and *Schinopsis balansae*) extract is an important source of natural polymers for leather tanning and adhesive manufacturing. We combined established phyto- and synthetic chemistry perspectives with electrospray mass spectrometry experiments to prove that quebracho proanthocyanidin polymers consist of an homologous series of flavan-3-ol based oligomers. The starter unit is always catechin which is angularly bonded to fisetinidol extender units. By comparison of the MS² fragmentation spectra of the oligomer with product ion scans of authentic catechin and robinetinidol samples, we proved that quebracho extract contains no robinetinidol, as is often reported. Quebracho proanthocyanidins have acid resistant interflavanil bonds, due to the absence of 5-OH groups in fisetinidol, and the aDP cannot be determined via conventional thiolysis and phloroglucinolysis. We used the MS data to estimate a conservative (minimum value) aDP of 3.1.

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1. Introduction

The wild quebracho forests in the Gran Chaco region of Argentina, Bolivia, and Paraguay have been harvested for more than 100 years as an important source of vegetable tannins and timber. The timber is durable and extremely hard and the name quebracho is derived from the Spanish word *quebrahacha* which means “axe-breaker”. To obtain a warm water soluble quebracho extract, the heartwood is stripped of its bark, chipped, and extracted with boiling water. A cold water soluble extract (sulfited extract) is obtained upon treatment of the warm water soluble extract with bisulfite or direct extraction of wood chips with a boiling aqueous bisulfite solution. Higher extraction rates are obtained with boiling aqueous bisulfite solution than with boiling water alone.

Quebracho extract is obtained from *Schinopsis balansae* (red “chaqueno” quebracho, pure tannin content 20–21%) from the Eastern Chaco region and *Schinopsis lorentzii* (red “santiagueno” quebracho, pure tannin content 15–18%) from the Western Chaco region. These two species were previously referred to as *Quebracho colorado chaqueño* and *Quebracho colorado santiaguense* (*Schinopsis quebracho-colorado*) and belongs to the family Anacardiaceae. A third tree species, *Aspidosperma quebracho-blanco* of the family Apocynaceae, is commonly referred to as white quebracho.

Quebracho extract consists of about 95% proanthocyanidins (PAs) and 5% water soluble sugars on a dry basis. The term proanthocyanidin (PA) refers to the characteristic development of a red color upon heating PAs with dilute acid (Roux, 1992). PAs are also referred to as condensed tannins to distinguish them from hydrolysable tannins which do not produce a red color when heated with aqueous acid. Hydrolysable tannin oligomers are esters of gallic acid and D-glucose. Important industrial sources of PAs are mimosa bark extract (*Acacia mearnsii*) and quebracho heartwood extract, and of hydrolysable tannins, tara pods, chestnut bark, and oak gall extracts.

Progress in defining quebracho PA composition has been slow, mainly due to the complexity of the extracts and the difficulty of isolating pure PAs with silica gel based chromatography materials. Uncertainties include different hydroxylation patterns of the constituent flavan-3-ol aromatic rings, different configurations at the C-2, C-3 and C-4 stereogenic centers, the possibility of a second ether interflavanil bond (A-type PAs), the average chain length (degree of polymerization), and the presence of angular oligomers.

Progress is further hampered by the absence of 5-OH groups in the constituent monomers, which imparts stability to the interflavanil bond against acid hydrolysis (Roux and Paulus, 1962; Roux et al., 1975). This renders the classical method to analyse PAs via acid hydrolysis of the interflavanil bond and subsequent trapping of intermediates with toluene- α -thiol or phloroglucinol (thiolysis and phloroglucinolysis) (Thompson et al., 1972; Foo and Porter, 1978; Kennedy and Taylor, 2003; Rigaud et al., 1991) and analysis

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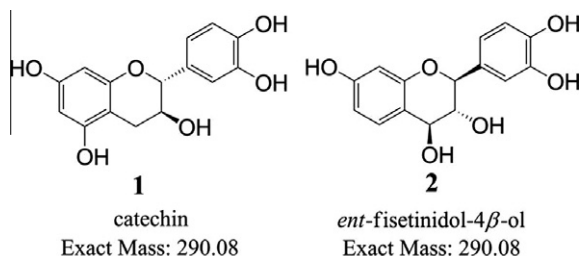


Fig. 1. Flavan-3-ol and flavan-3,4-diol monomers from the heartwood of *S. lorentzii* (putative building blocks of quebracho PAs).

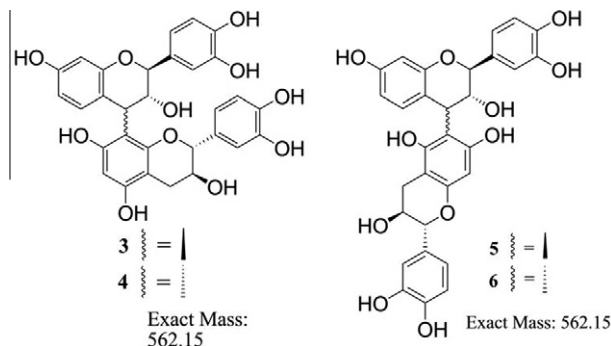


Fig. 2. Quebracho dimers from *S. balansae*.

of such trapped intermediates with HPLC (Shen et al., 1986; Koupai-Abyazani et al., 1993; Rigaud et al., 1991; Kennedy and Taylor, 2003), unreliable. Vivas et al. (2004), for example, failed to isolate any known flavan-3-ol toluene- α -thiol adducts upon thioacidolysis of quebracho tannins.

Most of the properties and industrial applications of vegetable tannins are attributed to the ability of the constituent PAs or hydrolysable tannins to form complexes with proteins via hydrogen bonds (Haslam, 1974, 1988, 1997). This includes astringency in tea and red wine (interactions between tannins and protein based taste receptors in the mouth) (Bate-Smith, 1954; Hofmann et al., 2006), anti-feeding properties (the indigestibility of tannin–protein complexes) (Hagerman et al., 1992), and growth inhibition of many micro-organisms (irreversible deactivation of enzymes) (Akin, 1982). Complexation of vegetable tannins with hide proteins transform biodegradable raw hide into leather which resists bacterial degradation, has a nice touch and is abrasion, heat, and water resistant (Haslam, 2005). Quebracho is extensively used to produce vegetable tanned leather. It is also used to manufacture adhesives via cross linking of the nucleophilic aromatic A-rings of the constituent PAs with formaldehyde (Pizzi, 1978). It is a source of oenological tannins, used to enhance the “mouth feel” properties of young or poor quality red wines. The absence of the 5-OH group and corresponding stability of the PA oligomer to interflavan-yl bond fission (Roux and Paulus, 1962; Roux et al., 1975) is probably an important factor in the industrial application of quebracho and mimosa PAs as it imparts longevity to leather and adhesives manufactured from it. A better understanding of the molecular composition of vegetable tannins will assist industrial applications. The relative affinity for collagen, rate of penetration into hides and skins during commercial tannage, mobility within leather, and desorption from finished leather under moist conditions are determined by oligomer composition (Covington, 2009). The availability of nucleophilic centers for cross linking with formaldehyde on the periphery of oligomers determines curing time and pot life of thermosetting PA based adhesives.

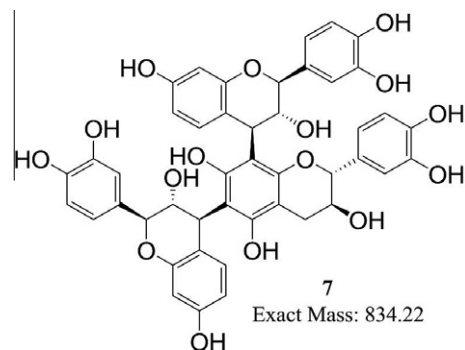


Fig. 3. Trimer isolated from *S. balansae* [*ent*-fisetinidinol-(4 β $\rightarrow$ 8)-catechin-(6 $\rightarrow$ 4 β)-*ent*-fisetinidinol].

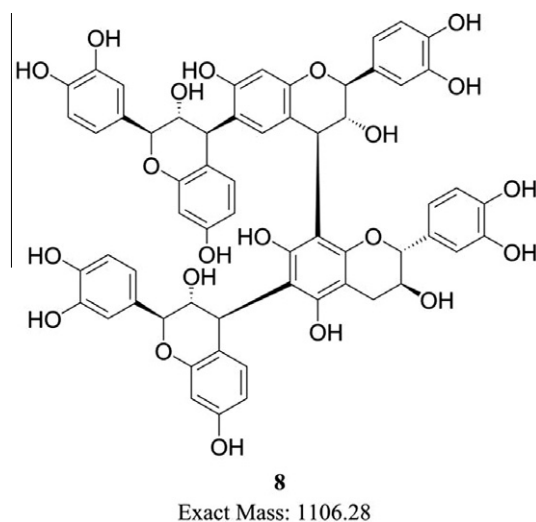


Fig. 4. Tetramer synthesized by Viviers and co-workers.

Electrospray ionization (ESI) and matrix-assisted laser desorption/ionization (MALDI) are soft ionization techniques that can fractionate a mixture of oligomers, such as quebracho PA extract, into fractions of different degrees of polymerization (DP) and estimate the average degree of polymerization (aDP). Soybean seed coat extract (Takahata et al., 2001) and hop PAs (Taylor et al., 2003) with a DP of 30 and 22, respectively, have been characterised by MALDI-TOF MS, and litchi PAs with a DP of 22 (Le Roux et al., 1998) with ESI. Moulis and co-workers (2011) compared aDP values obtained from thiolysis of PAs with the aDP values obtained from ESI-MS. They confirmed that poorer ionization of high DP PAs led to the underestimation of the aDP with MS, but concluded that ESI is appropriate to analyse low molecular weight PA samples (aDP below 20).

Pasch et al. (2001) investigated commercial sulfited quebracho tannin extract using MALDI-TOF mass spectrometry and observed oligomers to a maximum of decamers (2798 Da) (c.f. octamers for mimosa PAs). This is in line with the aDP of 6.74 (c.f. 4.9 for mimosa PAs) found by Thompson and Pizzi (1995) and Fechtal and Riedl (1993) with NMR methods. The individual PA oligomers consisting of clusters of ions 16 Da apart, was attributed to combinations and permutations of fisetinidinol (274 Da) and robinetinidinol (290 Da) constituent units. They concluded that quebracho PAs consist mostly of profisetinidins. The same authors claim that quebracho PAs were, in contrast with angular mimosa PAs, linear and that this linear structure explains the relative ease with which quebracho PAs undergo acid catalysed hydrolysis compared to smaller, less viscous oligomers.

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