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Tara tannins as phenolic precursors of thermosetting epoxy resins

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ABSTRACT

Tara pods powder was used as a phenolic source in the synthesis of thermosetting epoxy polymer. The tannase-assisted hydrolysis of galloylquinic acids contained in tara powder allowed the determination of the tannins hydroxyl value (13.7 mmol/g powder). Then, galloylquinic acids were reacted with epichlorohydrin and an aqueous solution of sodium hydroxide in the presence of benzyltriethylammonium chloride as phase transfer catalyst (PTC). The 1D and 2D NMR analyses of glycidylated products revealed the galloylquinic esters hydrolysis and the dimerisation of the glycidylated gallic moities. The glycidylated derivatives of tara tannins (**GETT**) were cured in epoxy polymer with isophorone diamine (**IPD**). The glass transition temperature (T_g = 129 °C) and the thermal resistance (T_{d30} = 294 °C) of the resulting network were determined. Preliminary results showed that this new epoxy polymer based on **GETT** displayed interesting properties which are close to those of the epoxy polymer formulated with commercial diglycidyl ether of bisphenol A (**DGEBA**).

1. Introduction

Tannins are phenolic compounds of relative high molecular weight. They are classified as condensed and hydrolysable tannins. The hydrolysable tannins are readily hydrolysed by acids, alkalis or enzymes into a sugar or a related polyhydric alcohol (polyol) and a phenolic carboxylic acid [1]. Depending on the nature of the phenolic carboxylic acid, hydrolysable tannins are subdivided into gallotannins and ellagitannins [1b,2]. They are biosynthesised by galloyltransferases as defence compounds (against Chinese gall and Turkey gall) and are accumulated in mesophyl cell walls [3]. The simplest hydrolysable tannins are gallotannins that are made up of gallic esters of glucose, shikimic acid, quinic acid and quercitol among others [4]. These tannins are found in various plants and trees such as chestnut, oak, sumac, and tara [5]. Tara (*Caesalpinia spinosa*) is a small leguminous tree native of Peru and widely spread in Latin America, from Venezuela to northern Chile [6]. The fruit of tara contains approximately 65% of pods [7] and 32–38% of seeds. From the pods, tara powder (100–200 mesh) is obtained by simply mechanically milling and sifting the gross powder. Afterward, this powder is mixed with water (4–5 parts of its weight) and heated at 65–70 °C for 30–40 min. After decantation and filtration, tara extract is obtained by atomisation. This ecological and economical procedure produces tara extract with high tannins content [8]. It has been reported that 40–65% of the fruit composition of *C. spinosa* corresponds to gallotannins [7]. The chemical structures of these gallotannins were widely investigated

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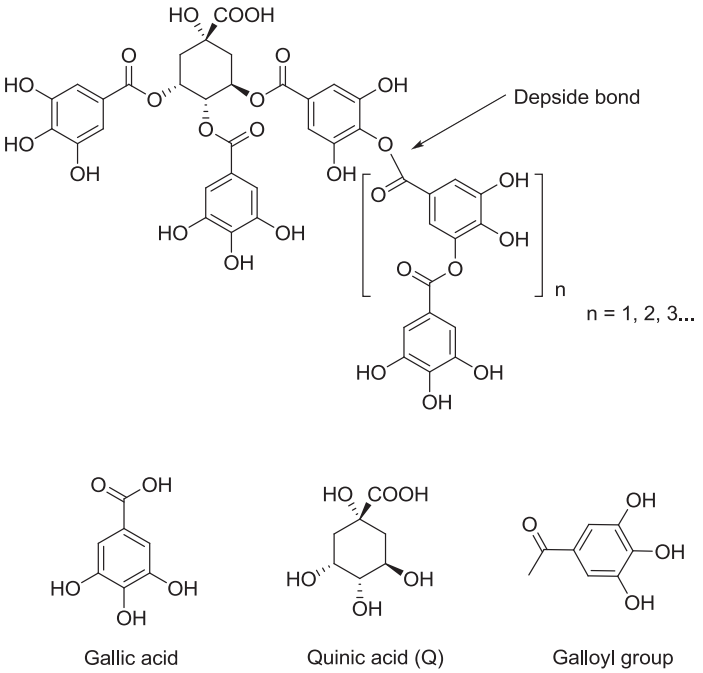
by Haslam et al. [9] and Horler et al. [10] who demonstrated that the principal components of tara tannin were based on a galloylated quinic acid structure (Scheme 1). Thus, they differ from members of hydrolysable tannins group which are based upon a galloylated or ellagoylated hexose. In galloylquinic acids, not only may gallic acid moieties be linked to each of the four hydroxyls carried by quinic acid but these may form aryl ester(s) (depsides) with one or more additional gallic acid moieties [9a,11]. Chains of up to three gallic acid moieties, of which two are depsidic, have been reported [9b], and a given quinic acid may bear more than one depside chain [12]. In such structures, depsidic linkages may be either *meta* or *para*.

Recently, Giovando et al. [13] reported the MALDI-TOF structural analysis of a tara tannins extract. It has been found that this extract is composed of a series of oligomers of polygallic acid (depsidic bonds) attached by an ester link to one quinic acid hydroxyl. Furthermore, other polygallic chains linked to one or two repeating units such as caffeic acid and methylated quinic, methylated gallic and methylated caffeic acids have been found in very small amounts [13]. The same research group has also demonstrated that tara tannins are constituted of a small amount of an ellagic unit that is surrounded by several gallic acid units. In addition, the ellagic acid contains an ester group which could be generated from hydrolysis reactions, during the extraction process [5].

Tara tannins find valuable applications in the food and beverage industries to clarify and give astringency to wine, tea, coffee, cacao, and other food. Thanks to their astringent properties and very light colour, tara tannins are particularly appreciated in the tannery industry [14]. Moreover, the alkaline hydrolysis of tara pods yields nearly 25% of gallic acid [15]. This phenolic acid and its decarboxylated form (pyrogallol) are extensively used in straining leather and hair and also as ingredients of developer in photography and printing inks [16]. Furthermore, they possess a large range of biological activities, including, antioxidant, antibacterial, antiviral, analgesic etc. [17], allowing them to act as precursors for the commercial production of drugs [18]. However, little attention has been given to the exploitation of these gallotannins as substitutes of phenolic compounds in thermosetting polymers manufacturing. Indeed, in 1973, as a consequence of the first oil crisis, Norsechem, a Norwegian paint group subsidiary in Malaysia that produces phenol formaldehyde resins, was forced to substitute 33 wt% of phenol with chestnut tannins extract in their formulations [19]. Once the first oil crisis had passed and the price of phenol became affordable again, the phenol formaldehyde–chestnut tannin resin production was stopped. Recently, phenolic resin wood panel adhesive based on chestnut tannins has been developed by Spina et al. [20]. In the same way, Garro et al. have used tara pods as starting material to produce phenol formaldehyde adhesives [14a]. Our laboratory, interested in developing of thermosetting epoxy resins from bio-sourced polyphenols [21] is considering tara tannins extract as a potential substitute of petroleum-based phenols in the formulation of epoxy polymers. Indeed, epoxy resins are the prime constituents in many adhesives, paints, coating, sealants and electronic materials [22]. Nevertheless, almost 90% of the world production of epoxy resins involves the use of non-renewable hazardous compounds such as bisphenol A. Meanwhile, there is a lack on the studies devoted to the use of tannins in the production of epoxy resins.



Scheme 1. Supposed tara tannins chemical structure.