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4 to 5 pages

Characterization of Algerian Eucalyptus tannins for a potential use in resin and foam formulation.

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Abstract

Increasingly high demand for composite materials is being recorded, creating a dilemma, especially for researchers. For some time now, a lot of work has been done on bio-sourced resins, derived from local plants such as eucalyptus in order to replace synthetic resins in the production of composites.

Recently, there has been a growing interest in tannin resins for their low cost and also for their availability. Tannins are natural phenolic compounds, which have been extensively researched for the development of a wide range of industrial applications.

First, the Algerian Eucalyptus tannins have been extracted by varying different extraction times, extraction temperature, solvent concentration, stage extraction and liquid-solid ratio. The the phenolic composition of Algerian Eucalyptus barks was studied. FTIR (Fourier Transformed Infrared Spectroscopy), NMR (Nuclear Magnetic Resonance) and TGA/DSC (Thermogravimetric analysis were used to examine Eucalyptus tannins. Analyzes showed that Eucalyptus barks are rich in condensed tannins, especially in procyanidin and prodelphinidin tannins. The reactivity to formaldehyde test (Stiasny number) showed the possible use of Eucalyptus tannins in resine and foam formulation.

Keywords: Eucalyptus, tannin, resin, foam, NMR, FTIR, TGA.

1. Introduction

Eucalyptus belongs to the myrtaceae family tree from Tasmania, Australia, fast- growing, generally blue-green, oval or very elongate, with mature fruits forming a drt, brown cone [1]. Some species, notably E. globulus, have been introduced to Europe, where they have acclimatized very well to the Mediterranean shores, as well as to Portugal, where huge eucalyptus forests have been planted for pulp production. . These species have also been planted in North Africa, including Morocco, Algeria, Tunisia and Libya. They are also found in the islands of Madagascar, Mayotte, Malta and Reunion, Sri Lanka, South Africa, on the slopes of Mount Elgon in Uganda, California, Argentina, Brazil, Chile, in Ecuador and Peru [2].

Tannins are one of the natural products which are widely distributed in plant kingdom, they are composed of different phenolic compounds [3]. Tannins are generally classified into two major types: hydrolysable tannins and condensed tannins, the hydrolysable tannins are mixture of simple phenols and it has had medicinal and cottage applications[4]. Condensed tannins are polymeric phenolic compounds comprising from flavon-3-ol repeating units; Condensed tannins are known for their wide distribution in various softwood and hardwood, and it constitute about 90% of the total world production of commercial tannins [5].

This study aims to evaluate, for the first time, the potential use of Algerian Eucalyptus barks tannins in resin and foam formulation.

For this purpose, polyphenolic, hydrolysable tannins and condensed tannins of Algerian Eucalyptus barks were analyzed using spectrometric and thermal methods. Eucalyptus tannins extraction was optimized. Then, Eucalyptus tannin- basedresin and foam was elaborate.

2. Materials and methods

2.1. Materials

Eucalyptus barks were harvested in different regions in Algeria and ground using a grinder with a screen of 0,4 mm diameter. The resulting powder was kept in darkness at room temperature (Saad, Khoukh et al. 2014) to conduct the follow-ing analyses described in Section 2.2.

2.2. Methods

To estimate the polyphenolics, the condensed tannins and the hydrolysable tannins contents in Eucalyptus barks, we exploited conventional and standard methods commonly used in the study and the determination of plants polyphenolic composition[6]. It comes to colorimetric methods developed as below.

Extraction of tannins for FTIR, NMR and TGA

Tannin extraction from Algerian Eucalyptus barks was carried out in water containing 2% of sodium bisulfate and 0,5% of sodium bicarbonate, with a sample-to-water ration equal to 1/5. The bark powder was immersed in water under continuous magnetic stirring for 6h at 70°C. The tannins extract so obtained, was filtred and dried in an oven at 50°C to yield tannins.

2.2.1. FTIR spectra analysis

Infrared analysis was performed using a Perkin Elmer Spectrum One equipped with a ATR- FTIR module. A few milligrams of milled product were deposited on the crystal (Diamond/ZnSe). The sample was crushed using the module for 10 scans and the scanning wave-length of infrared was 4000-400 cm^{-1} at a resolution of 4 cm^{-1}.

2.2.2. NMR analysis

NMR analysis was carried out on the ^{13}C carbon atom, in liquid phase. The spectra were recorded on brüker avance 400 MHz spectrometer. The chemical shifts were calculated relative to TMS ‘tetramethylsilan). The spectra appear at 100.6 MHz. the number of scans and the acquisition time were 1.36s and 12.000, respectively.
Tannin extract was dissolved in DMSA-d6 (deuterated dimethyl sulfoxid).

2.2.3. Thermogravimetric analysis

Thermal decomposition was performed using a TA instrument (TGA Q50 instrument). The temperature program was from 15 to 400 °C at a heating rate of 5°C/min. The measurements were conducted under air (60mL/min).

3. Results and Discussion

3.1. FTIR analysis of the Eucalyptus tannin extract

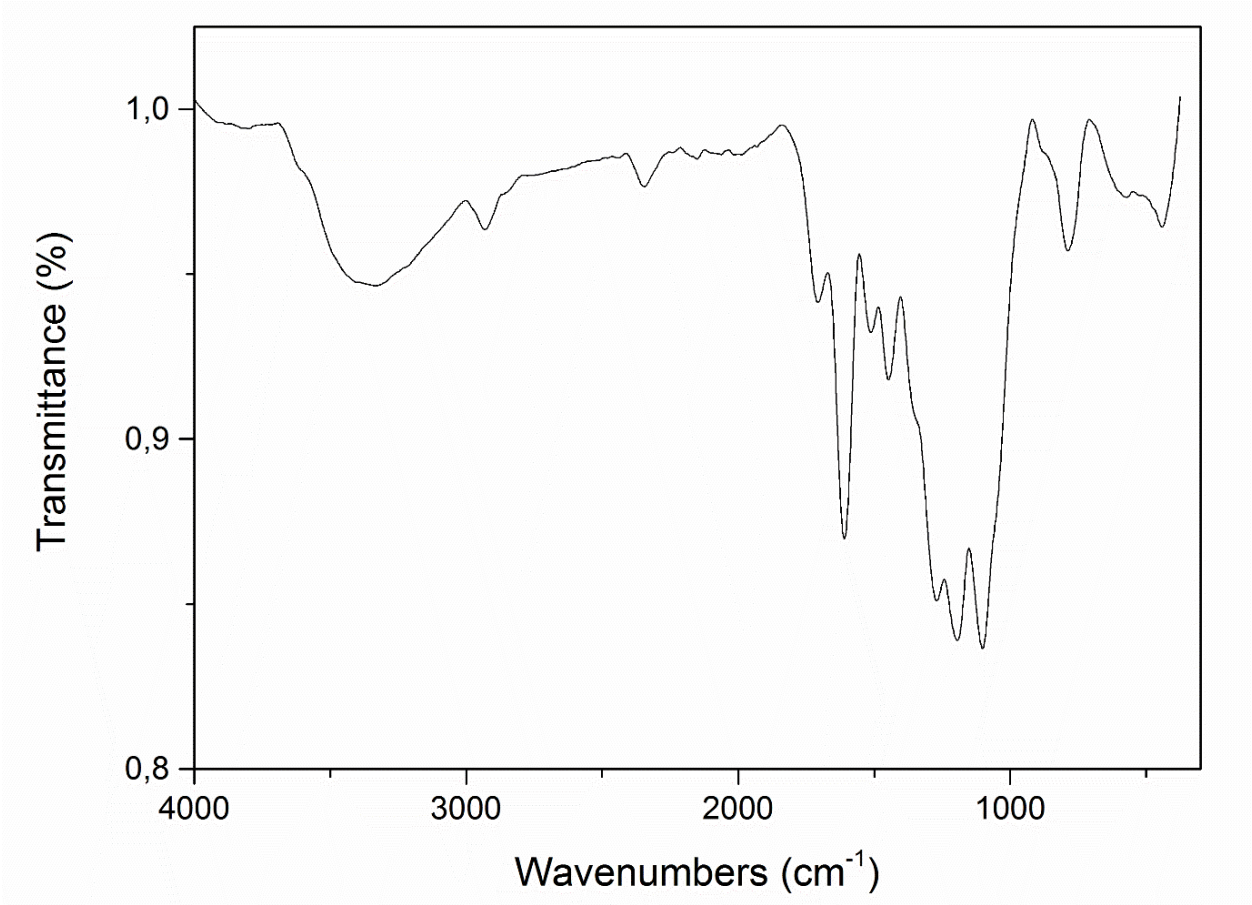

Fig.1. FTIR spectrum of Algerian Eucalyptus bark extract

The IR spectrum of Eucalyptus tannins extract is recorded in the 400-4000 cm $^{-1}$ region and is presented in Fig.1. The 3277 cm $^{-1}$ absorption bnd is attributed to –OH stretching vibration [7]. The band at 2930 cm $^{-1}$ is due to –CH and –CH_2 vibration of aliphatic hydrocarbon [7, 8]. The bands at 1610 cm $^{-1}$, 1520 cm $^{-1}$ and 1444 cm $^{-1}$ are assigned to aromatic ring stretching vibration. The 1030-1225 cm $^{-1}$ absorption bands including the C-O-C symmetrically stretching vibration, the aromatic CH in-plane bending vibrations, the glucose ring vibration and the hollocellulose and hemicelluloses CO stretching vibration [4]. The band at 1370 cm $^{-1}$ is attributed to phenolic stretch vibration of –OH and aliphatic –CH deformation in methyl groups. This band is commpn to lignins which could mean that lignins are present in the Eucalyptus bark extract [4]. According to [9] , bands at 1110 cm $^{-1}$ and 1283 cm $^{-1}$ show the presence of condensed tannins. These bands can be assigned to the ethereal CO asymmetric stretching vibration arising from the pyran-derived ring structure of condensed tannins.

3.2. NMR analysis

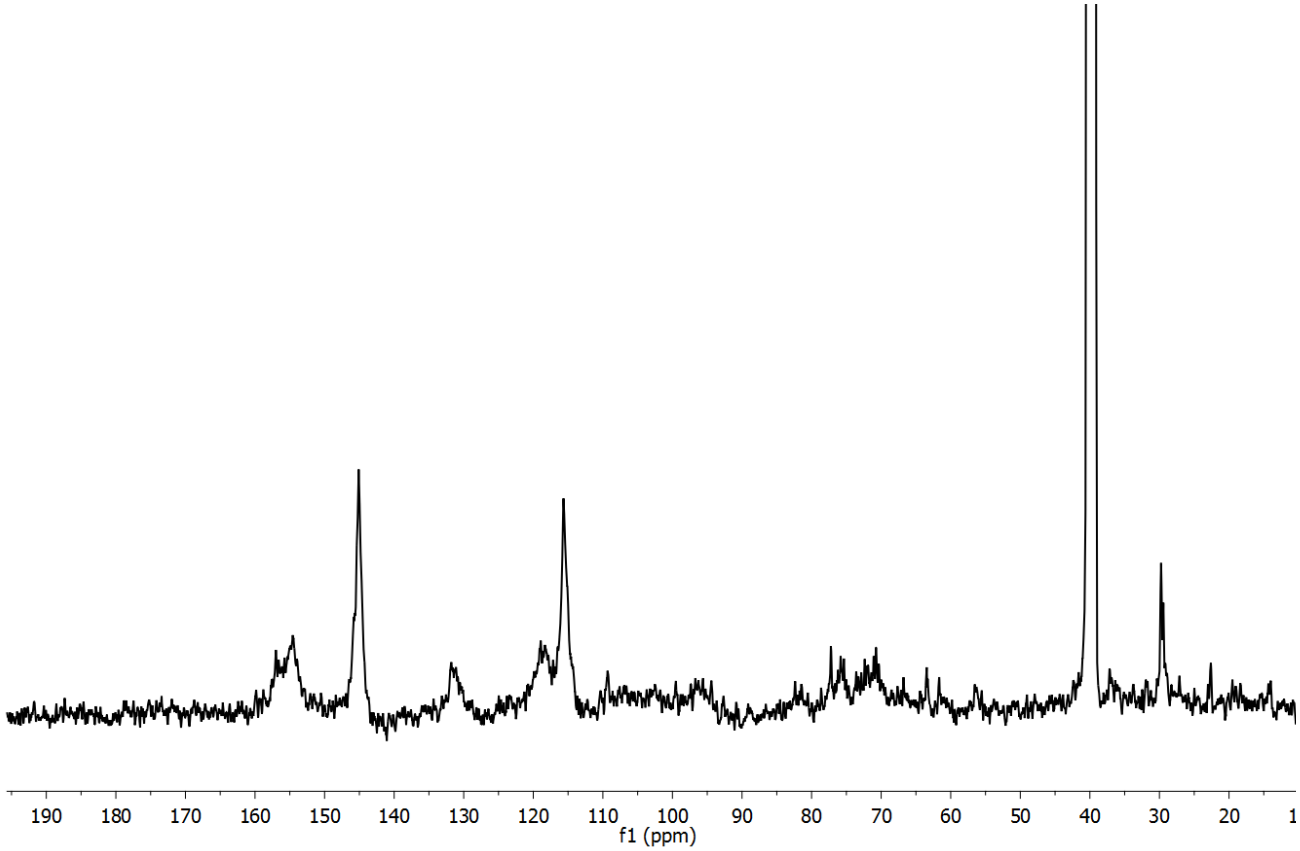

Fig.2. 13C- NMR spectrum of Algerian bark tannins extract in DMSO-d6

The interpretation of 13C-NMR spectrum (Fig.) was based on research conducted by Fu et al.,2007[10]; Zhang and Ming Lin 2008[11]; Zhang et al.,2010[12] and Ping et al., 2012[7].

Typical condensed tannin signals, containing Procyanidin (PC) and Prodelphinidin (PD) units, with more PC that PD. The minor amount of PD is observed by the small peak at 131.4ppm (C4').

According to Pizzi 1994[13], PC units are detected with the following signals:

- 115ppm-120ppm: C2', C5' and C6'
- 115 ppm: C3' and C4'
- 150ppm -160ppm: C5,C7 and C8a

PD units are detected with the following signals:

- 130.8 ppm: C4' overlapping the chemical shift of C1
- 90 ppm-110ppm: C8,C6,C6' and C2'
- 60-85ppm: Carbohydrates.

According to Gutzeit et al.,2007 and Castillo-Muonoz et al.,2009; fraction of sugars are detected at: 101.8 -102.8 ppm: C1 "; 71.4-77.1 ppm: C2 ", C3 " and C5 ", 68.7-71.4 ppm: C4 " and 60.6-61.1 ppm: C6 ",these displacements could be due to the hydrolysable tannins, to the presence of flavanols. [14, 15]

According to Ucar et al., 2013, the bands between 70-90ppm are due to the stereochemistry of the PC uinity ring C: C2 Cis with peaks between 75-76ppm and C2 Trans with peak at 82 ppm. [16]

According to Cren-Olive et al.,2002 the signal at 29.4ppm is attributed to Catechin C4 or to a terminal Flavanol unit when the neighboring C3 carries a hydroxyl group.[17]The 13C spectrum of Algerian eucalyptus tannin is different from that of pomegranate rich in hydrolysable tannins which shows strong signals between 60-100 ppm [18], while it is close to that of Pinus Brutia with a predominance in tannins condensed as well as Kandelia Candel species with a predominance of the isomer Cis.[11, 16]

3.2. Thermogravimetric analysis of the tannin extract

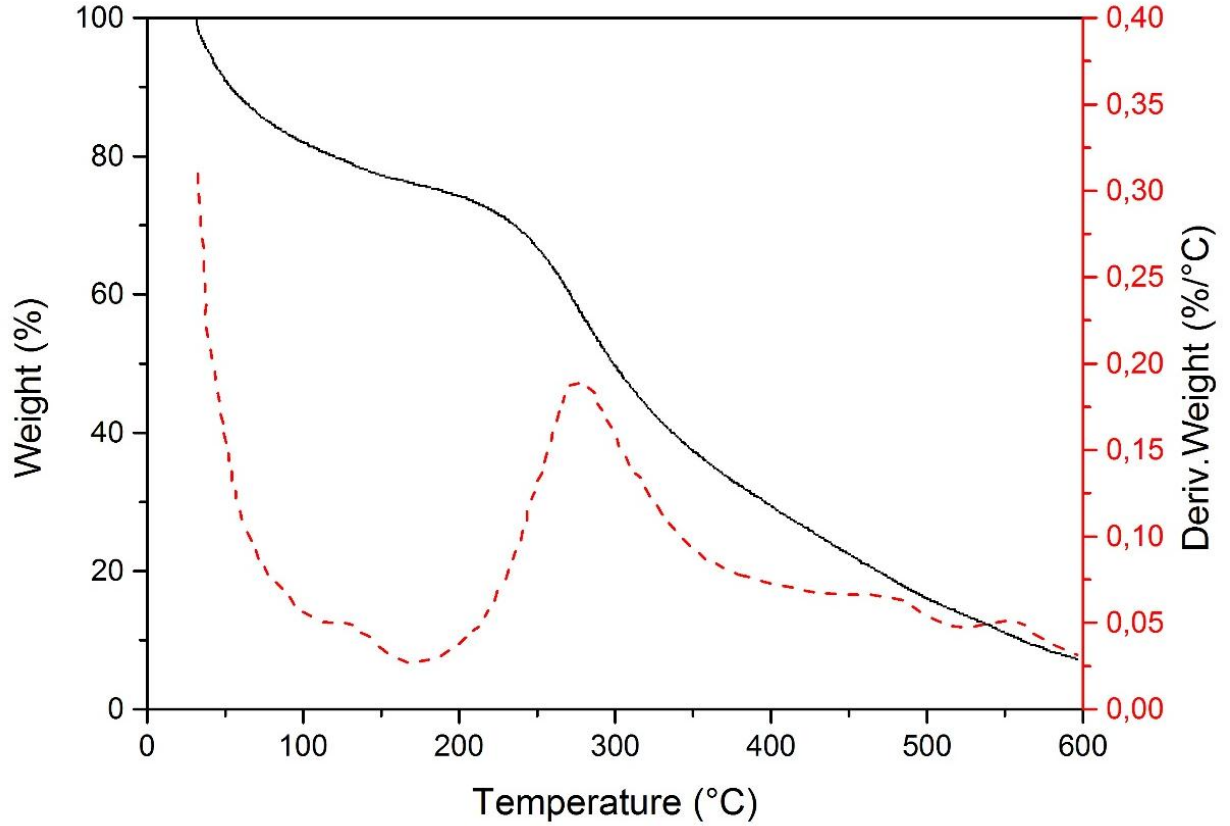

Fig.3. The TGA (black) and DTGA (red) thermograms of Algerian Eucalyptus tannins heated at 10°C/min under Nitrogen.

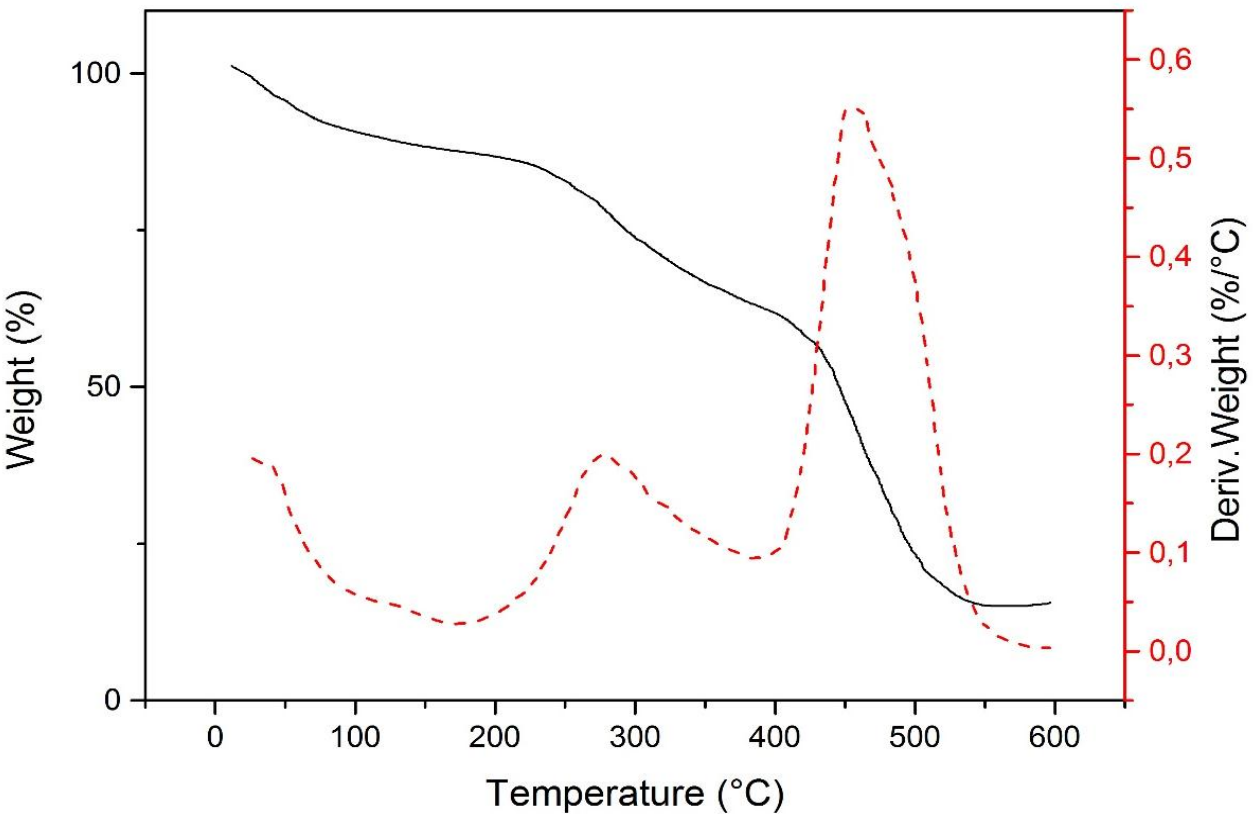

Fig.4. The TGA (black) and DTGA (red) thermograms of Algerian Eucalyptus tannins heated at 10°C/min under air.

The thermogram of the analysis carried out on the tannin Eucalyptus of Algeria conducted under nitrogen, Fig.3 shows two mass loss typical of thermal phenomena.
The first is attributed to the loss of absorbed moisture mass and is equivalent to 10%.
The second loss, which is more significant, corresponds to the decomposition of the tannin, the decomposition of the eucalyptus tannin begins at 169 ° C, the peak of the latter appears at 275°C, the residue at the end of the decomposition is equal to 53%.
Eucalyptus tannins are then more stable than the condensed tannins of radiata pine, which begins to degrade at 150 ° C [19].
Compared to the hydrolyzable tannins of pomegranate peels[20] which begin to degrade at 149°C and have a decomposition peak at 190 ° C with a residue rate of 36.4% under the same conditions. analysis eucalyptus tannins are more stable.
This result is explained in the work of Saad 2013, as being caused by the presence of a large amount of carbohydrate in the pomegranate peel extract, mainly due to the presence of sugar in the structure of the hydrolysable tannins.[18]
Algerian eucalyptus tannins are thermally stable compared to Schinopsis Quebracho-colorado tannin, which has decomposition peaks at 249.9 ° C with a residue level of 55.29% [21].
Fig.4 shows the thermal behavior of Algerian eucalyptus tannin under air.
The degradation of eucalyptus tannin begins at 156 ° C, the TGA thermogram shows three decompositions (156 ° C, 350 ° C and 470 ° C), a catechol and catechol formation that characterize the degradation of condensed tannins can be driven by pyrolysis [22].
Garro et Galvez, 1992 during a study on the thermal decomposition of gallic acid observed a decomposition in three stages[5]

- The first corresponding to decarboxylation (release of carbon dioxide) during heating at 260 ° C (26.27%);
- The second may be caused by additional loss of hydroxyl at 308 ° C (29%);
- The last at 503 ° C (45%) is due to the significant oxidation of the residual carbon (CO2, H2O, CO).

In the case of the Algerian eucalyptus tannin of our study the different stages of the thermal decomposition depend essentially on the structure, the composition, the degree of polymerization as well as the nature of the interflavonoid bond.

4. Conclusion

We have analyzed for the first time the tanniferous composition of Algerian Eucalyptus barks for resin and foam formulation. Colorimetric essays showed that Algerian Eucalyptus barks are richer in condensed tannins than in hydrolysable tannins. This result has been confirmed by FT-IR analysis. We have clearly observed by ^{13}C NMR analysis that Algerian Eucalyptus tannins are of procyanidins and prodelphinidins types. Thermogravimetric analysis revealed the thermal stability of Eucalyptus tannins extract than radiat pine, quebracho and mimosa tannins.

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