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Benoit Ndiwe, Antonio Pizzi, Beda Tibi, Raidandi Danwe, Noel Konai, et al.. African tree bark exudate extracts as biohardeners of fully biosourced thermoset tannin adhesives for wood panels. Industrial Crops and Products, 2019, 132, pp.253-268. 10.1016/j.indcrop.2019.02.023. hal-03138365

# HAL Id: hal-03138365 https://hal.science/hal-03138365

Submitted on 22 Oct 2021

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## 1 African tree bark exudate extracts as biohardeners of fully biosourced

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# thermoset tannin adhesives for wood panels

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### 16

## ABSTRACT

A totally "bio" hardener derived from the exudate extract of the African trees Vachellia 17 nilotica and Senegalia senegal was investigated. It hardened a maritime pine tannin resin 18 without any obvious presence of an aldehyde thus obtaining a completely "bio" adhesive for 19 wood panels. MALDI-ToF and CP MAS <sup>13</sup>C NMR analysis indicated that the hardeners 20 cross-linking species was 2,5-dihydroxymethyl furan linked onto carbohydrate chains. The 21 hydroxymethyl furan moieties reacted both after detachment from the carbohydrate chains but 22 also with carbohydrate chains still attached. The carbohydrates too were then involved as part 23 of the binder. The gel times were slower than what was obtainable with paraformaldehyde but 24 sufficiently fast to possibly be of industrial significance. 25 Keywords: "bio" hardeners, bioadhesives, wood adhesives, Vachellia nilotica, Senegalia 26

*senegal seval*, exudates, 2,5-dihydroxymethyl furan, carbohydrate oligomers

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# 29 **1. INTRODUCTION**

Tannin adhesives for wood panels and their derivatives have now been used industrially for
many years in a number of countries especially from the southern emisphere (Plomley 1966;
Pizzi 1978, 1982, 2006, 2013, 2016, 2017; Sealy Fisher and Pizzi 1992; Pizzi et al 1994;

Pichelin et al 2006; Moubarik et al 2010; Ping et al 2011; Valenzuela et al 2012; Navarrete et 33 al 2012; Abdullah and Pizzi 2013; Zhou et al 2013, 2017; Santoso et al 2016; Santiago-34 Medina et al 2016; Santos-Ucha et al 2017; Shirmohammadi et al 2018; Ghahri and Pizzi 35 2018a,b) but also in some Asian countries (Pichelin et al 2006) and even occasionally in 36 European countries. Over the years, starting from their early commercial utilization, in the 37 search for more effective or more environment friendly systems, a number of different 38 hardeners have been tried and used plus or minus successfully for these adhesives. Among 39 these paraformaldehyde (Pizzi, 1978, 1982), formalin solution (Carter Holt Harvey 1974-40 41 1989; Pizzi and Sorfa 1979), resorcinol or phenol-formaldehyde resols (Plomley 1973), 42 hexamine (Pizzi 1994, Pichelin et al 2006), trishydroxymethylnitromethane (known also as 2-43 nitro-2-(hydroxymethyl)-1,3-propanediol) (Trosa and Pizzi 2001), 2-amino-2-(hydroxymethyl)-1,3-propanediol (Grigsby et al 2008), glyoxal (Ballerini et al 2005; 44 45 Navarrete et al 2010a), and a variety of different aldehydes (Pizzi 1983, Pizzi et al 1980; Rossouw et al 1980; Bohm et al 2016), and even tannin autocondensation (Meikleham et al 46 47 1994; Pizzi et al 1995; Pichelin et al 2006) have been tried and used. Only in three cases, and quite recently, fully biohardeners have been used to yield 100% bioadhesives from tannins, 48 49 with some degree of success, these being hydroxymethyl furfural (Santiago 2018), furfuryl alcohol (Trosa and Pizzi 1998; Abdullah 2013) and vanillin and its derivatives (Santiago et al 50 2016). The former gave particleboards that although not reaching the internal bond (IB) 51 52 strength requirements of relevant standards showed nonetheless some promise for the future. 53 The second reached the requirements of the standards but marginally, the furfuryl alcohol behaving more as a copolymerization partner than just a hardener. The last one instead gave 54 acceptable IB strength results when using a fast reacting procyanidin tannin, such as pine 55 tannin, but at this stage is too expensive for industrial optimization, although increased 56 57 production for other purposes may decrease its cost in future.

58 Considering the above, the search is still on for a biohardner which can be effective for tannin adhesives while presenting an acceptably low cost. Recently, extracts from some African tree 59 60 barks, fruits and sap have shown promise for such an application. Senegalia senegal (known 61 also as Acacia senegal) is a small tree known by different popular names, such as Gum 62 acacia, Gum arabic tree, Sudan gum and Sudan gum arabic. In India, It is known as Kher or Khor in India (Pervez et al 2009). It is native to semi-desert regions of Sub-Saharan Africa, as 63 64 well as Oman, Pakistan, west coastal India. It grows to a height of 5–12 m, with a trunk up to 30 cm in diameter. Vachellia seyal (also known as Vachellia nilotica, Acacia seyal or Acacia 65 nilotica) as Senegalia senegal, is a tropical african thorny tree of the Fabaceae family, 66

67 Mimosoideae subfamily, which can reach 10 meters of height and parts of which are 68 traditionally used in the countries of origin for a number of applications. Recently, it was 69 noticed that extracts of the bark, exudates and fruits from these and similar species were 70 capable of reacting with local tannins.

As these materials are relatively inexpensive the work presented here addresses first of all the interest in trying to use them as hardeners of tannin extracts under different conditions. Secondly, it aims to analyse them to identify what could be the active chemical and its mechanism of reaction that could allow them to be used as tannin adhesives biohardners. The third aim was to prepare fully natural thermosetting wood panel adhesives, and to evaluate their effectiveness.

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#### 78 **2. EXPERIMENTAL**

#### 79 **2.1.** Extraction

For both *Vachellia nilotica* and *Senegalia senegal* from the Dacheka forest in the extreme northern region of Cameroun the bark of the tree was hurt by incisions and from the wound came out a complex organic solution of high viscosity called an exudate.

The locality of Dacheka is located in the Extreme-North Cameroon region, a semi-arid 83 Sahelian tropical region with an aridity index between 0.20 and 0.50 (Onana, 2018) where the 84 ambient temperature is very high, reaching more than 40 ° C in March. This type of 85 ecosystem is characterized by the non-availability of soil water with low rainfall, the annual 86 87 rainfall being 811mm. The harmattan wind blows from October to March. The heart of the dry season is in January. Southwest winds appear timidly in June, before bringing rain in 88 89 August and especially in September. This climate favors the cultivation of Vachelia nilotica and Senegalia senegal, cotton and cereals. Depending on the season, the landscape is 90 91 characterized by savannah, grassland and prickly steppe.

92 The exudates were collected and dried at 37°C for 21 days. Finally, the dried exudates were
93 crushed to obtain a soluble whitish powder easier to stock and to use.

94 The pine (*Pinus pinaster*) tannin bark extract used as resin was a pure tannin obtained from
95 DRT (Derivés Resiniques et Terpeniques, Dax, France) and characterized previously
96 (Navarrete et al 2010b, 2013).

97 **2.2. Gel Time** 

The gel test for a tannin resin is performed as follows: 10 g of the reaction mixture composed 98 of pine tannin or a tropical Acacia tannin as a 50% solution in water to which the hardener has 99 been added in proportion by weight Tannin solids : Hardner = 5:1. The solution is placed in a 100 test tube and this is placed in a water bath, maintained at boiling temperature (100°C) at 101 102 normal atmospheric pressure. A wire spring is inserted in the test tube and rapidly moved up and down and the time to gelling is measured by stopwatch. The test is done in duplicate and 103 the average value is reported. This test is a standard FESYP (European Federation of Panels 104 Manufacturers) test and is usely extensively in Europe for wood adhesives (FESYP 1979). 105

106 **2.3.** MALDI-TOF analysis

Samples for Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) analysis 107 were prepared first dissolving 5mg of sample powder in 1mL of a 50:50 v/v acetone/water 108 109 solution. Then 10 mg of this solution is added to 10µL of a 2,5-dihydroxy benzoic acid (DHB) matrix. The locations dedicated to the samples on the analysis plaque were first 110 covered with 2µL of a NaCl solution 0.1M in 2:1 v/v methanol/water, and predried. Then 1µL 111 of the sample solution was placed on its dedicated location and the plaque is dried again. 112 MALDI-TOF spectra were obtained using an Axima-Performance mass spectrometer from 113 Shimadzu Biotech (Kratos Analytical Shimadzu Europe Ltd., Manchester, UK) using a linear 114 polarity-positive tuning mode. The measurements were carried out making 1000 profiles per 115 sample with 2 shots accumulated per profile. The spectrum precision is of +1Da. 116

117

118 **2.4**.

#### 2.4. CP-MAS 13C NMR Spectra

119 The exudates extracts were analyzed by solid state CP MAS <sup>13</sup>C NMR. Spectra were obtained 120 on a Brüker AVANCE 400 MHz (Brüker, Billerica, MA, USA) spectrometer with a 4 mm 121 probe at a frequency of 12 kHz. The pulse duration at 90° was 4.1  $\mu$ s, with a contact time of 2 122 ms and a recycling delay of 4s. Chemical shifts were determined relative to tetramethyl silane 123 (TMS) used as control. The spectra were accurate to 1 ppm. The spectra were run with 124 suppression of spinning side bands.

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#### 126 **2.5.** Thermomechanical Analysis (TMA)

127 The resins were tested by thermomechanical analysis. The samples were prepared by applying 128 each adhesive at a surface spread of 200 g/m<sup>2</sup> of liquid adhesive between two beech wood

decorative plies of average density 0.750 g/cm<sup>3</sup>, of moisture content of 11%, and of with 129 dimensions of 21mm × 6mm × 1.1mm. The beech wood plies were very smooth as these were 130 cut from decorative veneers of 0.5 mm thickness. These beech-resin-beech sandwiches were 131 tested in non-isothermal mode between 25°C and 250°C at a heating rate of 10°C/minute with 132 a Mettler Toledo 40 TMA equipment (Mettler-Toledo, Zurich, Switzerland). They were tested 133 in three-point bending on a span of 18 mm exercising a force cycle of 0.1/0.5 N on the 134 specimens, with each force cycle of 12 seconds (6s/6s). The classical mechanics relationship 135 between force and deflection 136

137  $E = [L^3/(4bh^3)][F/(\Delta f_{wood} - \Delta f_{adhesive})]$ 

where E is Young's modulus, L = the length of the span tested, b and h are respectively the 138 width and the thickness of the specimen, F is the force exerted on the tested assembly,  $\Delta f_{wood}$ 139 and  $\Delta f_{adhesive}$  are the deflections that have been proven to be constant and reproducible (Pizzi 140 1997; Pizzi et al 1997). The formula allows the calculation of the Young's modulus E by 141 measuring the change in deflection amplitude of the tested sandwich between the initial and 142 final equilibrium deflections (Pizzi 1997; Pizzi et al 1997), for each case tested. Such a 143 measuring system has been introduced and is used to follow the progressive hardening of the 144 adhesive with the increase of temperature and to indicate comparatively if an adhesive system 145 is faster or slower hardening and if it gives stronger joints than another one. 146

147

#### 148 **2.6.** Particleboards preparation and testing

Three identical monolayer particleboards were prepared using the following glue mix: 100 g 149 of purified maritime pine (Pinus pinaster) tannin was dissolved in water to yield a 150 151 concentration of 40%-45% solids. The pH was corrected to 7 with NaOH solution at 33% concentration. To this were added 10 g (10% solids on solids) Vachellia nilotica exudate 152 153 extract powder. The glue mix was applied at a level of 10% by weight of adhesive solids content calculated on dry industrial pine wood chips. The wood chips were at a moisture 154 155 content of 2%. The panels were hot pressed at 220°C, for 7.5 minutes with a pressure cycle of 2.7MPa/1.47MPa/0.5MPa for 2 min/2.5 min/3 min respectively. The panels prepared were 156 157 35x35x1.4 cm size. After cooling each panel was conditioned at a temperature of 20°C at 65% relative humidity to reach an equilibrium moisture content of 12% and then cut and 5 158 159 samples each of 5 x 5 cm size for each panel were tested for dry internal bond (IB) strength 160 according to European Norm EN319 (1993). Proof of bonding performance is known to be

best measured in particleboards by measuring the internal bond (IB) strength. The IB strength 161 162 is measured by a tension test perpendicular to the plane of the panel according at 2 seconds per mm separation rate and according to European Norm EN319. Control panels using an 163 industrial urea-formaldehyde (UF) resin (Georgia-Pacific LEAFC2 resin) of molar ratio urea 164 to formaldehyde of 1:1.08, solids content of 66%, viscosity at 20°C of 450 mPa.s and pH of 165 7.8 were also pressed under the identical conditions. The adhesive was applied at the same 166 resin load level, so that the results could be compared. Ammonium sulphate hardener solution 167 was added to the UF adhesive at the weight ratio of 2% solid ammonium sulphate on total 168 169 adhesive solids content.

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### 3. RESULTS AND DISCUSSION

The series of gel time results shown in Figs. 1 indicate that addition of the exudates of *Vachellia nilotica* or *Senegalia senegal* to either an African extracted bark tannin or to a well codified pure maritime pine tannin extract yield rapid gel times, well in the range usable for wood panel adhesives.

176

#### Please insert here Figure 1

Of particular interest are first of all the comparison of the shape of the gel time curves 177 obtained using these hardeners to cure a pure pine tannin extract Their trend is characteristic 178 of the gel time trend of phenolic materials, markedly accelerating as one passes from pH 4 to 179 pH 9. Moreover, the gel times at pH 9 is around 50 seconds at 100°C for pure maritime pine 180 tannin hardened with paraformaldehyde and around 350 seconds for the same tannin hardened 181 with the raw exudate from either Vachellia nilotica or Senegalia senegal (Fig. 1). Even much 182 183 more marked differences can be observed at the other pHs tested, with the difference increasing as the pH used shifts towards the pH of mimimum reactivity of the pine tannin. 184 185 Thus, comparing the results and the shape of the get time curves at different pHs the mechanism of hardening caused by the exudate extract on pure pine tannin appears to be 186 187 different from that of an aldehyde (Fig. 1), one main characteristic being that the exudatecaused gel time is much slower than the paraformaldehyde one at all pHs but particularly at 188 189 the pH of lower reactivity (Fig. 1). This already indicates that the conceiled hardener involved in the exudate is not likely to be an aldehyde as its chemical behavior is rather different.. 190

191

Please insert here Figure 2a,b

The first indication of what can be the structure of the exudate is obtained by CP MAS <sup>13</sup>C
NMR (Fig. 2a,b). There are different species that respond to the NMR signals present but the
most likely one is species I.



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196

For species I the furan nuclei C3 shift is calculated at 108 ppm (experimental 109 ppm) and 197 its C4 is calculated at 80 ppm (experimental 82 ppm) (Pretsch et al 1989). The shifts between 198 72 and 98 ppm are the region of carbohydrates (the central peak characteristic of all sugars), 199 with the considerable width of the peaks indicating that these are carbohydrate oligomers of 200 some sort (Perlin and Hamer 1979; Idstrom et al. 2016). The C=O of an ester is at a shift 201 calculated at 173 ppm (experimental 176 ppm) (Pretsch et al 1989, Wehrli and Wirtlin 1978). 202 The C-OH attached to the furan ring C2 is calculated at 99 ppm (experimental = 104 ppm), 203 meaning that there is another molecule possibly linked to this (Species II) (BioRad 204 205 Laboratories 1999).



206

207

Thus, for species II the branching carbon attached to the furan C2 has a calculated shift at 82.6 ppm (experimental 82.6 ppm), with the C attached to the next sugar through a glycosidic linkage being foreseen at a calculated 60 ppm (experimental 62 ppm) (BioRad Laboratories 1999). It must be pointed out that species I and II are observed in the MALDI spectra (Fig. 3a,b,c,d,e; peaks structure assignements in Table 1), the first at 304 Da (calculated 306 Da) and the second at respectively a calculated and experimental value of 495 Da. (Figs. 3) and the equivalent peak at 522 Da.

216

#### Please insert here Figure 3a,b,c,d,e and Table 1

However different species could occur with the same NMR shifts but presenting a differentstructure, namely



With species III being confirmed by the MALDI peak at 325 Da (exp 326 Da) thus 302 MW+ 222 23 Na<sup>+</sup>. Species IV could exists too but at 300+23 = 323 Da is more far from the 223 experimental 326 Da in Fig 3b. While in presence of moisture often the aldehyde groups are 224 in the form of  $-CH-(OH)_2$  this does not appear to be the case because the specimen was dry 225 and there is no aldehyde group shift observed in the NMR of the compound indicating that 226 structure IV is highly unlikely. Thus, it is structure III that is the one that is most probable to 227 occur.

228 A species of type V could also be immagined



V

229

230

Species V, would equally present the C3 and C4 of the furan ring both at a calculated shift of
80 ppm (experimental 82 ppm), and the CH<sub>2</sub> of the ether linkage at 70 ppm (exp. 71 ppm)

- 233 (Pretsch et al 1989). However, no species of this type is observed in the MALDI spectra, thus
- 234 its presence is really unlikely. A species of type VI can also be present,



VI

235

#### 236

with the furan C3 = 108 ppm (exp 109 ppm) C4 80 ppm (exp 82 ppm) C=O of ester 173 ppm (exp 176 ppm) (Pretsch et al 1989), sugar carbons between 72 and 98 ppm (the central peak characteristic of all sugars) (Idstrom et al 2016; Lagel et al 2016). The CH<sub>2</sub> of the furanic hydroxymethyl function is foreseen at 57 ppm (experimental 62 ppm) for both furan and sugars, species VI being observed also in the MALDI as 290+23 (Na<sup>+</sup>) = at a calculated 313 Da (experimental 313 Da).

243 What starts to become clear from the above is then that the biohardeners are composed of a carbohydrate chains, for example short glucose chains, possibly hemicellulose fragments, 244 245 onto which are linked furanic moieties that hydrolyze under certain conditions to obtain a hydroxyl furfuryl alcohol analogues, such as 5-hydroxy-2-hydroxymethyl furan (VII) and 2,5-246 dihydroxymethyl furan (VIII). This species presents C3 shift at 80 ppm (experimental 82 247 ppm), C4 shift at 108 ppm (experimental 109 ppm), the CH<sub>2</sub> of the hydroxymethyl function 248 being foreseen at 57 ppm (experimental 62 ppm) for both furan and sugars (Pretsch et al 249 1989; BioRad laboratories 1999; Idstrom et al 2016; Lagel et al 2016). The species is also 250 found at 137 Da (138 Da experimental) with Na<sup>+</sup> in the MALDI analysis (Fig 3a). 251





VII

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As well as the species at 151 Da (experimental 150 Da) with Na<sup>+</sup>, the species without Na+ also being noticed at 128 Da (calculated and experimental) (Fig. 3a).



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VIII

Other two species could occur but their MW with and without Na<sup>+</sup> MALDI enhancer are
further away from the values present that are 128 Da and 151 Da (exp 150 Da). These are



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Which present respectively 124 Da (IX) and 126 Da (X) without Na+ and 147 and 149 Da with Na+. The first is definitely not occurring, but the second at 126 and 149 Da might also occur although is not noticed in further analysis.

265

Several oligomers presenting the same <sup>13</sup>C NMR shifts but at higher molecular weight can be
identified by MALDI ToF. Thus as the species XI to XV.

268 Thus by MALDI at 496 Da (exp 495 Da) in Fig. 3c the species XI responding to the same

269 NMR shifts can be identified (without Na<sup>+</sup>)

270



XI

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The structure of the species at 617 Da experimental (calculated 617 Da) with Na+ =594
MW+23 =617 Da (Fig. 3c,d).



XII

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As well as species XIII at 622 Da (exp 619 Da) without Na<sup>+</sup> (Fig. 3d)



XIII

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280 The species at 785 Da (calculated and 786 Da experimental) without Na<sup>+</sup> is visible in Fig. 3d.

281 This is oligomer XIV.



282

283

284 This later structure (XIV) is a mix of  $\beta$ -D glucuronic acid (the two higher units) with 285 methylglucuronic acid as the lower unit. These type of linkages alternate with glucose to 286 glucose linkages in short chains. The equivalent structure XV due to a mix of just three  $\beta$ -D

287 glucuronic acid units is also possible at the same 785 Da (Fig. 3d).



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XV

And equally the structure XVI at 799 Da calculated (exp. 801 Da) without Na<sup>+</sup> and at 847 Da

calculated (exp 845 Da) (Fig. 3d,e).



293

292

XVI

- And species XVII at 882 MW+23 = 905 Da (Exp. 903 Da) and equally with an -OH substituted by an -OCH3 thus at 917 Da (with Na+) (experimental 918 Da) and with two -
- OH groups substituted by –OCH3 is represented by the peak at 932 Da (Fig. 3e).



297

298

XVII

That presents itself also as a repeating tract of oligomer at 910 MW+23 = 933 Da
(experimental and calculated) (Fig. 3e).



301

302

As well as species XVIII at 896 MW+23 (Na<sup>+</sup>) = 919 Da (exp 919 Da) as well as species XIX with two hydroxymethyl furan reactive function at 911 MW+23 = 934 Da exp and calculated (Fig. 3e).

XVIII



XIX

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307

All this appears to indicate what is the mechanism of action of the biohardeners tried. Thus, there are oligomers of different types all yielding 5-hydroxy-2-hydroxymethyl furan and 2,5dihydroxymethyl furan which are then the real hardening molecules. It cannot be excluded however that the free, reactive hydroxymethyl furan functions of furan moieties linked to the carbohydrate chains may be able to react as such, bringing the attached carbohydrate chain in the reaction as well.

#### 314 The reactions being schematically, for example



Carbohydrate chains with and without furan moieties attached The oligomer shown above also occurs in Fig. 3e at 882 + 23 (Na<sup>+</sup>) = 905 Da (903 Da exp) and equally with an –OH substituted by an –OCH<sub>3</sub> thus at 917 Da (with Na<sup>+</sup>) (experimental 918 Da) and with two –OH groups substituted by –OCH<sub>3</sub> is represented by the peak at 932.8 Da.

In Fig. 3a are also noticeable oxidized hexoses, thus carrying a -COOH group, such as the one at MW 196 (exp. 198-199Da), and its equivalent 196+23 (Na<sup>+</sup>) = 219 Da (experimental

- 322 218 Da) and also the unit minus an -OH = 180 Da, this being a gluconic acid (Fengel and
- Wegener 1989) repeating unit. It occurs at 177.9-178.9 Da (exp.) in Fig. 3a.



324

325 Glucuronic acid (Fengel and Wegener 1989) MW 194, minus one –OH = 178 D as a

326 glucuronic acid repeating unit. It occurs at 193 Da experimental, and 178-179 Da exp.,

327 respectively.



328

Equally, Glucaric acid (Fengel and Wegener 1989), MW = 210 Da minus one -OH = 194 Da;
it occurs at 193 Da (exp). It exists also at 210+23 = 233 Da , (exp 233 Da), as shown in Fig.
3a.



332 333

It is of primary interest to also determine if the 5-hydroxy-2-hydroxymethyl furan and the 2,5dihydroxymethyl furan, obtained by hydrolysis from the sugar oligomers carrying it, are the active hardeners of a tannin-based adhesive. To this purpose MALDI examination of pine tannin hardened by the biosourced *Vachelia nilotica* exudate extract was carried out to determine the structure of the oligomers and of the cross-linking that takes place onhardening.

340

### Please insert here Figure 4a,b,c,d and Table 2

In the condensation product the peak at 138 Da of the 5-Hydroxy-2-hydroxymethyl furan is 341 present as well as the peaks at 128 and 150 Da for the 2,5-dihydroxymethyl furan, together 342 with the peaks at 178 Da and 199 Da characteristic of some oxidized monocarbohydrates 343 (Fig.4a). From the condensed flavonoid tannin are present in Fig. 4b the monoflavonoid peaks 344 at 273 Da and 294 Da characteristic of a fisetinidin monomer respectively without and with 345 Na<sup>+</sup>; the peak at 290 Da characteristic of catechin and epicatechin, and the peaks at 304 Da 346 and 327 Da characteristic of a gallocatechin (delphinidin) monomer respectively without or 347 348 with Na<sup>+</sup> (Fig. 4b).



XX

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350

The species XX is present 384+23 = 407 Da (exp 406) (Fig. 4c). And 385 exp for 384 calculated without Na<sup>+</sup> In Fig. 4b describing the reaction products of the pine tannin with the exudate hardener. Equally, the presence of species XXI with Na+ 399+23 = 422 Da calculated (exp. 419-421 Da) (Fig. 4c) attests that the same reaction occurs with catechin

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XXI

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357

There are a number of different species which are formed by condensation of 2,5dihydroxymethyl furan with the tannin flavonoids. Thus,



361

XXII

## 362 Structure XXII at 663 Da (with Na<sup>+</sup>) is present (Fig. 4d).



363

364

XXIII

365 Structure XXIII at 656 Da (without Na<sup>+</sup>) is present (exp 655 Da), Fig 4d



- 366
- 367

Structure XIV is possibly the one contributing to the peak at 862 Da calculated (exp 859 Da),
Fig. 4e. Structures XXII, XXIII, XXIV show that cross-linking has occurred and that 2,5dihydroxymethyl furan is a rather reactive cross-linker for the pine tannin resin.

XIV

371

There are also flavonoid oligomers that have both reacted with 2,5-dihydroxymethyl furan, such as at 601 Da a dimer of catechin + Na<sup>+</sup>, and at 857 Da a fisetinidin-fidetinidin-catechin trimer +Na<sup>+</sup> (exp 858 Da). And at 656 Da without Na<sup>+</sup>, calculated and experimental, it is found a fisetinidin dimer having reacted with one 2,5-dihydroxymethyl furan and of structure XXV, with at 695 Da (with Na+) (exp. 697) a fisetinidin-catechin dimer reacted with one 2,5-dihydroxymethyl furan and of structure XXVI, and at 711 Da (with Na+) (exp 711-713) an equally reacted catechin dimer of structure XXVII (Fig. 4d,e).



380

Equally, flavonoid dimers reacted with 2 molecules of 2,5-dihydroxymethyl furan are also present. For example, the peak at 789 Da (with Na<sup>+</sup>) (exp 787 Da) (Fig. 4d,e) could corresponds a structure of the type



XXVIII

384

A very small proportion of species in which the furan moiety is still linked to a carbohydrate also appear to occur, such as fisetinidin-catechin dimer at 848 Da (exp. 847 Da), the latter presenting structure XXIX (Fig. 4e).



XXIX

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390

Thus, the real hardener present in the exudate extract of the African tree species *Vachellia nilotica* and *Senegalia senegal seyal* is 2,5-hydroxymethyl furan both detached from the sugar chains carrying it as well as still attached to the carbohydrate residues carrying it.

After defining the molecular species involved it is wise to test the bonding capability of the 394 combination of a pine tannin resin with the biohardeners. First the systems were tested by 395 thermomechanical analysis. Thermomechanical analysis methods have been developed over 396 many years to determine more rapidly the potential effectiveness of different adhesives 397 systems, experimental or not (Pizzi 1997; Kamoun et al 1998; Lecourt et al 2003). Thus, 398 thermomechanical analysis was first carried out to initially explore the potential of such new 399 400 adhesive systems. Wood particleboard panels bonded with the combination of biohardener and bioresin were then prepared. The results obtained are shown in Fig. 5 for the TMA and in 401 Table 3 for the internal bond (IB) strength of the particleboard. 402

403

#### Please insert here Figure 5 and Table 3

404 In Fig. 5 the TMA results indicate that the best performance judged by the highest value of MOE obtained (Kamoun et al 1998; Lecourt et al 2003) is when the tannin is used at pH 7. 405 Pine tannin is so reactive that it is used at pHs near to its lower reactivity (pH 4.2-4.5) when 406 using a fast hardener such as formaldehyde (Pizzi 1994). Thus, it appears logical that its 407 curing will be possibly slower with the biohardners. As the pH is higher pine tannin becomes 408 considerably more reactive, thus a pH of 7 is needed with the biohardeners. Equally, at pH 9 409 the reaction may start to be slightly too fast to yield optimal results. It is of interest to note 410 from Fig. 1 that the gel times at pHs 7 and 9 are not too different, with the one at pH 7 being 411 slightly slower, while at pH at 3.5 the gel time is very much slower. This notwithstanding, the 412 TMA results in Fig. 5 are rather good at all the three pHs tested. This is likely to be due to 413

different effects: at pH 3.5 the 2,5-dihydroxymethyl furan is the reactive species reacting with 414 the tannin, that instead is near to its minimal reactivity. At pH 9 instead the tannin is very 415 reactive possibly driving the reaction with the hardener. This is so because previous work has 416 indicated that furan hydroxymethyl functions react particularly well with tannin phenolic 417 nuclei at the low pH and high pH (Abdullah and Pizzi 2013). In Fig. 5 it is noticed that 418 reactivity depends from the temperature. At constant temperature increase as the TMA test is 419 done it can be noticed that (i) the slope of the curves, hence the rate of increase of the MOE is 420 more rapid both at pH 7 and pH 9, while it is slower for pH 3.5 and (ii) that the maximum 421 422 value of the MOE is reached when the adhesive system is at pH 7. At pH 9 the cross-linking reaction being too fast engenders a too rapid immobilization of the hardened network hence a 423 424 less cross-linked one. At pH 3.5 the reaction being slower, cross-linking is slower hence the network is weaker too. 425

Having thus determined by TMA the best pH conditions for using the adhesive this was tested by preparing laboratory particleboards. As proof of bonding performance is best measured by the internal bond (IB) strength test by European Norm EN319 the dry IB strength results are shown in Table 1. In Table 1 are also reported the results obtained by bonding wood panels under the same conditions with a synthetic, industrial urea-formaldehyde (UF) adhesive. The IB strength obtained using the experimental adhesive is comparable to that obtained with the control.

433

#### 434 CONCLUSIONS

Totally "bio" wood particleboard panels have been prepared with a totally "bio" adhesive 435 using as hardener of a maritime pine tannin adhesive the extract of exudates of the African 436 trees Vachellia nilotica and Senegalia senegal. The analysis of these showed that the reactive 437 species of these hardeners were furan hydroxymethyl species linked to carbohydrate 438 oligomers. These gave 2-hydroxy-5-hydroxymethyl furan and especially 2,5-dihydroxymethyl 439 440 furan, these second being the reactive species leading to cross-linking. The hydroxymethyl 441 furan moieties were shown to react both after detachment from the carbohydrate chains but 442 also with carbohydrate chains still attached, thus involving the carbohydrates too as part of the binder. The gel times were slower than what obtainable with paraformaldehyde but 443 444 sufficiently fast to possibly be of industrial significance.

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- 565
- Aknowledgements: The LERMAB of the University of Lorraine is supported by a grant
  overseen by the French National Research Agency(ANR) as part of the Laboratory of
- 568 Excellence (Labex) ARBRE.

570	Table 1. MALDI ToF peaks. Oligomers structures assignements for the exudates MALDI
571	spectra shown in Fig. 3.

128 Da	НООСОН
138-139 Da	HOOHNa*
150-151 Da	HO OH Na+
178-179 Da	Gluconic and glucuronic acid repeating units
193-194 Da	Glucuronic acid
198-199 Da	но
219 Da	HO
233 Da	Glucaric acid + Na <sup>+</sup>
304-305 Da	
313 Da	
326- 327 Da	HO OH OH







Table 2. MALDI ToF peaks. Oligomers structures assignements for the reaction of theexudates with a flavonoid tannin (Fig. 4).

128 Da	но он
138-139 Da	
150-151 Da	HO OH Na+
178-179 Da	Gluconic and glucuronic acid repeating units
198-199 Da	но
273 Da	Fisetinidin monomer
294-295 Da	Fisetinidin monomer + Na <sup>+</sup>
290 Da	Catechin and epicatechin monomers
304 Da	Gallocatechin (delphinidin) monomer
327 Da	Gallocatechin (delphinidin) monomer °Na <sup>+</sup>
385 Da	HO O OH HO OH
406 Da	HO O OH OH Na <sup>+</sup>
420-422 Da	HO, O, OH HO, O, OH OH OH
601 Da	Catechin dimer + Na+





608	
609	FIGURE LEGENDS
610	Figure 1. Comparison of the gel times at different pHs of a maritime pine tannin resin
611	hardened with the exudate extract of the african tree Vachellia nilotica vs hardening
612	with paraformaldehyde.
613	Figure 2. CP MAS <sup>13</sup> C NMR of (a) the exudate extract of <i>Vachellia nilotica</i> , and (b) of the
614	exudate extract of Senegalia Senegal seyal.
615	Figure 3. MALDI ToF of the exudate extract of Vachellia nilotica: (a) 20 Da-200 Da range.
616	(b) 200Da-400 Da range. (c) 400 Da – 600 Da range. (d) 600 Da – 800 Da range. (e)
617	800 Da – 1000 Da range.
618	Figure 4. MALDI ToF of the condensation of a maritime pine tannin resin with the exudate
619	extract of Vachellia nilotica: (a) 20 Da-200 Da range. (b) 200Da-400 Da range. (c)
620	400 Da – 600 Da range. (d) 600 Da – 800 Da range. (e) 600 Da – 900 Da range.
621	Figure 5. Thermomechanical analysis results at different pHs of the maritime pine bark
622	tannin resin during its cure with the exudate of Vachellia nilotica as hardener.
623	
624	
625	
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627	





## 636 Fig. 2b.



638 Fig. 3a







643 Fig. 3c







647 Fig. 3e



650 Fig. 4a



652 Fig. 4b.



654 Up Fig 4c, Down Fig. 4d





657 Fig. 4e



Fig. 5