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1 African tree bark exudate extracts as biohardeners of fully biosourced 2 thermoset tannin adhesives for wood panels

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15

16

ABSTRACT

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

26 **Keywords:** “bio” hardeners, bioadhesives, wood adhesives, *Vachellia nilotica*, *Senegalia*
27 *senegal seyal*, exudates, 2,5-dihydroxymethyl furan, carbohydrate oligomers

28

29 1. INTRODUCTION

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

33 Pichelin et al 2006; Moubarik et al 2010; Ping et al 2011; Valenzuela et al 2012; Navarrete et
34 al 2012; Abdullah and Pizzi 2013; Zhou et al 2013, 2017; Santoso et al 2016; Santiago-
35 Medina et al 2016; Santos-Ucha et al 2017; Shirmohammadi et al 2018; Ghahri and Pizzi
36 2018a,b) but also in some Asian countries (Pichelin et al 2006) and even occasionally in
37 European countries. Over the years, starting from their early commercial utilization, in the
38 search for more effective or more environment friendly systems, a number of different
39 hardeners have been tried and used plus or minus successfully for these adhesives. Among
40 these paraformaldehyde (Pizzi, 1978, 1982), formalin solution (Carter Holt Harvey 1974-
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-
44 (hydroxymethyl)-1,3-propanediol (Grigsby et al 2008), glyoxal (Ballerini et al 2005;
45 Navarrete et al 2010a), and a variety of different aldehydes (Pizzi 1983, Pizzi et al 1980;
46 Rossouw et al 1980; Bohm et al 2016), and even tannin autocondensation (Meikleham et al
47 1994; Pizzi et al 1995; Pichelin et al 2006) have been tried and used. Only in three cases, and
48 quite recently, fully biohardeners have been used to yield 100% bioadhesives from tannins,
49 with some degree of success, these being hydroxymethyl furfural (Santiago 2018), furfuryl
50 alcohol (Trosa and Pizzi 1998; Abdullah 2013) and vanillin and its derivatives (Santiago et al
51 2016). The former gave particleboards that although not reaching the internal bond (IB)
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
54 behaving more as a copolymerization partner than just a hardener. The last one instead gave
55 acceptable IB strength results when using a fast reacting procyanidin tannin, such as pine
56 tannin, but at this stage is too expensive for industrial optimization, although increased
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
59 adhesives while presenting an acceptably low cost. Recently, extracts from some African tree
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
63 Khor in India (Pervez et al 2009). It is native to semi-desert regions of Sub-Saharan Africa, as
64 well as Oman, Pakistan, west coastal India. It grows to a height of 5–12 m, with a trunk up to
65 30 cm in diameter. *Vachellia seyal* (also known as *Vachellia nilotica*, *Acacia seyal* or *Acacia*
66 *nilotica*) as *Senegalia senegal*, is a tropical african thorny tree of the Fabaceae family,

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.

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

77

78 **2. EXPERIMENTAL**

79 **2.1. Extraction**

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

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

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

106 **2.3. MALDI-TOF analysis**

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

117

118 **2.4. CP-MAS ¹³C NMR Spectra**

119 The exudates extracts were analyzed by solid state CP MAS ¹³C NMR. Spectra were obtained
120 on a Bruker AVANCE 400 MHz (Bruker, Billerica, MA, USA) spectrometer with a 4 mm
121 probe at a frequency of 12 kHz. The pulse duration at 90° was 4.1 µs, 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.

125

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/m² of liquid adhesive** between two beech wood

129 decorative plies of average density 0.750 g/cm³, of moisture content of 11%, and of with
130 dimensions of 21mm × 6mm × 1.1mm. The beech wood plies were very smooth as these were
131 cut from decorative veneers of 0.5 mm thickness. These beech-resin-beech sandwiches were
132 tested in non-isothermal mode between 25°C and 250°C at a heating rate of 10°C/minute with
133 a Mettler Toledo 40 TMA equipment (Mettler-Toledo, Zurich, Switzerland). They were tested
134 in three-point bending on a span of 18 mm exercising a force cycle of 0.1/0.5 N on the
135 specimens, with each force cycle of 12 seconds (6s/6s). The classical mechanics relationship
136 between force and deflection

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

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

147

148 **2.6. Particleboards preparation and testing**

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

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

170

171 3. RESULTS AND DISCUSSION

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

176

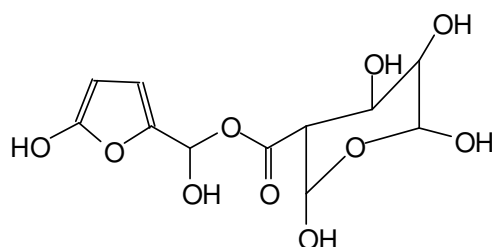
Please insert here Figure 1

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

191

Please insert here Figure 2a,b

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

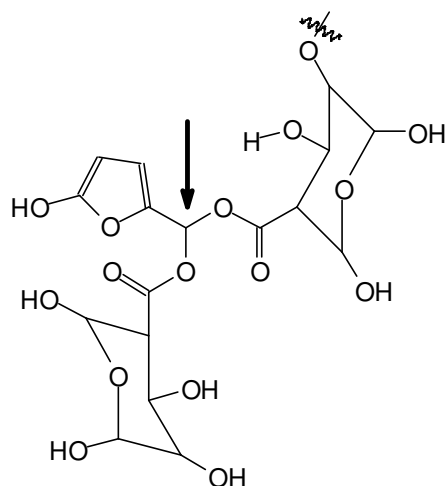


195

196

I

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



206

207

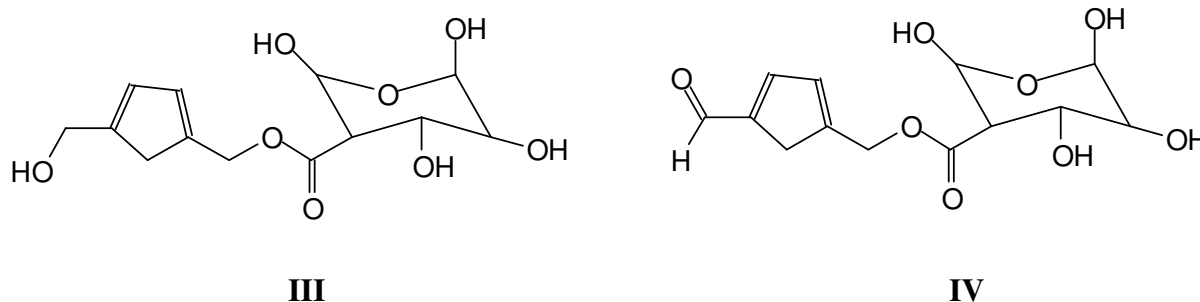
II

208 Thus, for species II the branching carbon attached to the furan C2 has a calculated shift at
209 82.6 ppm (experimental 82.6 ppm), with the C attached to the next sugar through a glycosidic
210 linkage being foreseen at a calculated 60 ppm (experimental 62 ppm) (BioRad Laboratories
211 1999).

212 It must be pointed out that species I and II are observed in the MALDI spectra (Fig.
213 3a,b,c,d,e; peaks structure assignments in Table 1), the first at 304 Da (calculated 306 Da)
214 and the second at respectively a calculated and experimental value of 495 Da. (Figs. 3) and
215 the equivalent peak at 522 Da.

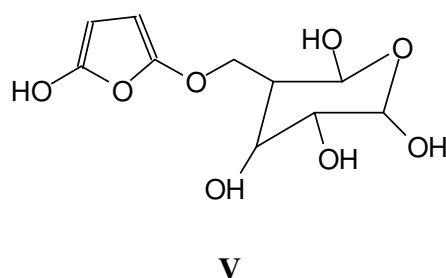
216 **Please insert here Figure 3a,b,c,d,e and Table 1**

217 However different species could occur with the same NMR shifts but presenting a different
218 structure, namely

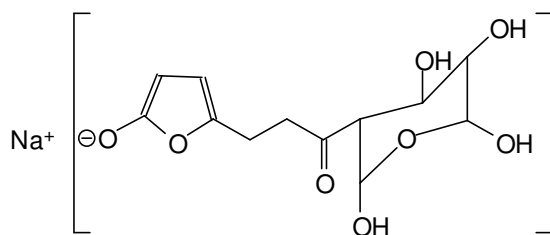


221 With species III being confirmed by the MALDI peak at 325 Da (exp 326 Da) thus 302 MW+
222 23 Na⁺. Species IV could exist too but at 300+23 = 323 Da is more far from the
223 experimental 326 Da in Fig 3b. While in presence of moisture often the aldehyde groups are
224 in the form of -CH-(OH)₂ this 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 imagined



231 Species V, would equally present the C3 and C4 of the furan ring both at a calculated shift of
232 80 ppm (experimental 82 ppm), and the CH₂ 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,



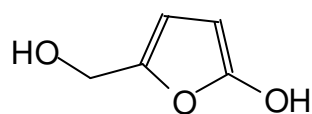
235

236

VI

237 with the furan C3 = 108 ppm (exp 109 ppm) C4 80 ppm (exp 82 ppm) C=O of ester 173 ppm
 238 (exp 176 ppm) (Pretsch et al 1989), sugar carbons between 72 and 98 ppm (the central peak
 239 characteristic of all sugars) (Idstrom et al 2016; Lagel et al 2016). The CH₂ of the furanic
 240 hydroxymethyl function is foreseen at 57 ppm (experimental 62 ppm) for both furan and
 241 sugars, species VI being observed also in the MALDI as 290+23 (Na⁺) = at a calculated 313
 242 Da (experimental 313 Da).

243 What starts to become clear from the above is then that the biohardeners are composed of a
 244 carbohydrate chains, for example short glucose chains, possibly hemicellulose fragments,
 245 onto which are linked furanic moieties that hydrolyze under certain conditions to obtain a
 246 hydroxyl furfuryl alcohol analogues, such as 5-hydroxy-2-hydroxymethyl furan (VII) and 2,5-
 247 dihydroxymethyl furan (VIII). This species presents C3 shift at 80 ppm (experimental 82
 248 ppm), C4 shift at 108 ppm (experimental 109 ppm), the CH₂ of the hydroxymethyl function
 249 being foreseen at 57 ppm (experimental 62 ppm) for both furan and sugars (Pretsch et al
 250 1989; BioRad laboratories 1999; Idstrom et al 2016; Lagel et al 2016). The species is also
 251 found at 137 Da (138 Da experimental) with Na⁺ in the MALDI analysis (Fig 3a).

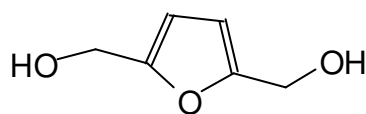


252

253

VII

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

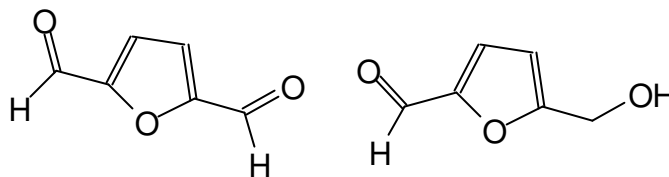


256

257

VIII

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



260

261

IX

X

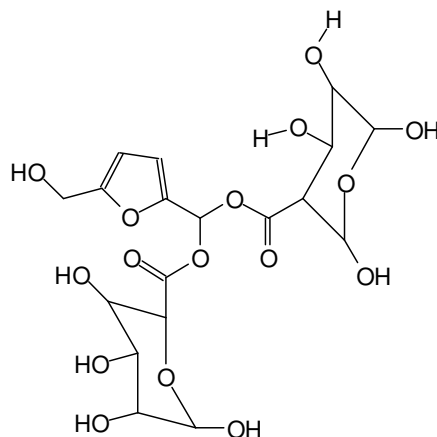
262 Which present respectively 124 Da (IX) and 126 Da (X) without Na⁺ and 147 and 149 Da
263 with Na⁺. The first is definitely not occurring, but the second at 126 and 149 Da might also
264 occur although is not noticed in further analysis.

265

266 Several oligomers presenting the same ¹³C NMR shifts but at higher molecular weight can be
267 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⁺)

270

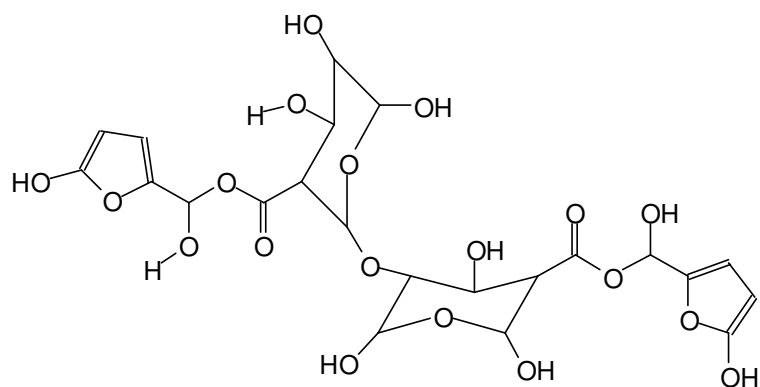


271

272

XI

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

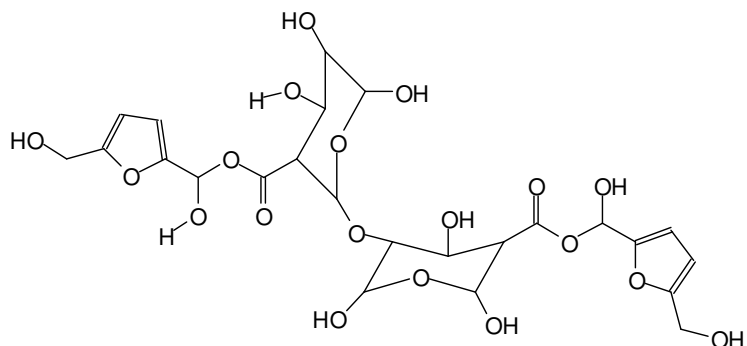


275

276

XII

277 As well as species XIII at 622 Da (exp 619 Da) without Na⁺ (Fig. 3d)



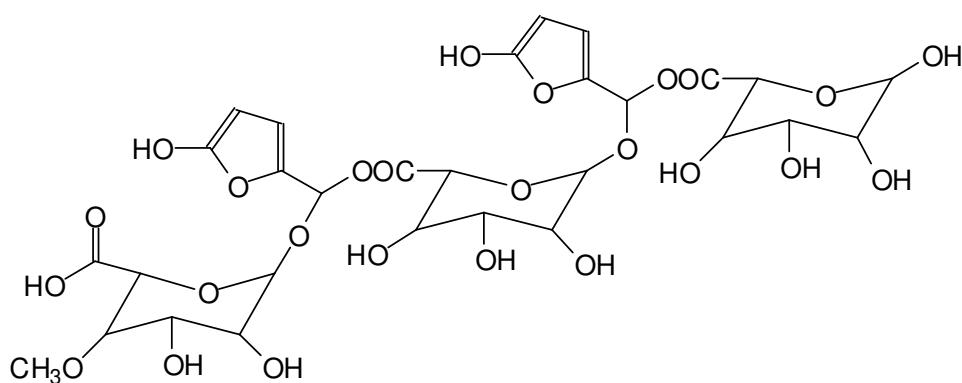
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279

XIII

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

281 This is oligomer XIV.



282

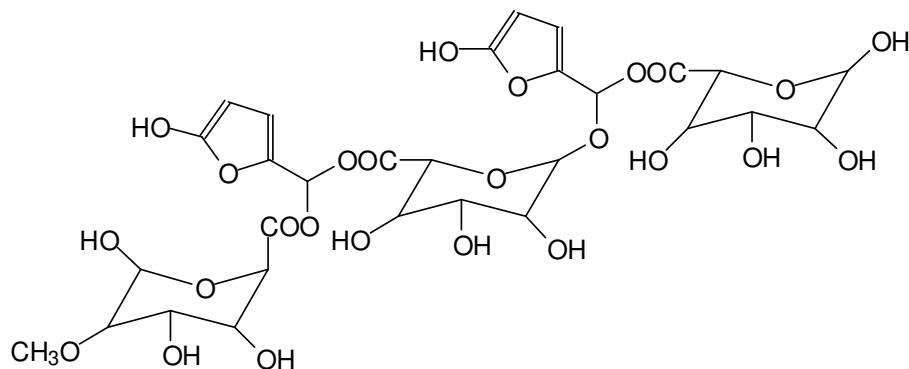
283

XIV

284 This later structure (XIV) is a mix of β -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 β -D
287 glucuronic acid units is also possible at the same 785 Da (Fig. 3d).

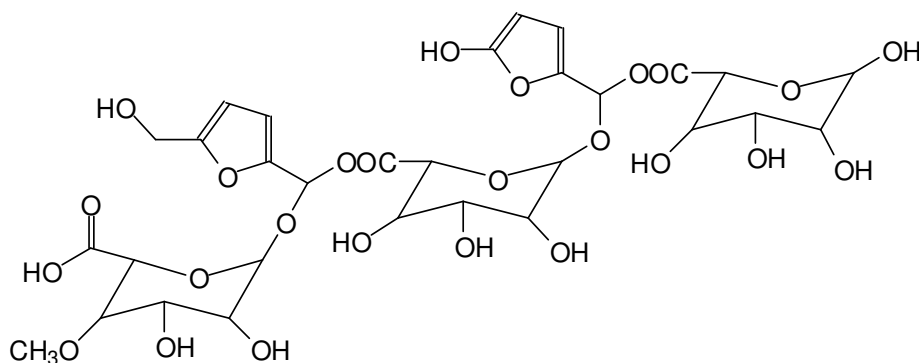


288

289

XV

290 And equally the structure XVI at 799 Da calculated (exp. 801 Da) without Na^+ and at 847 Da
291 calculated (exp 845 Da) (Fig. 3d,e).

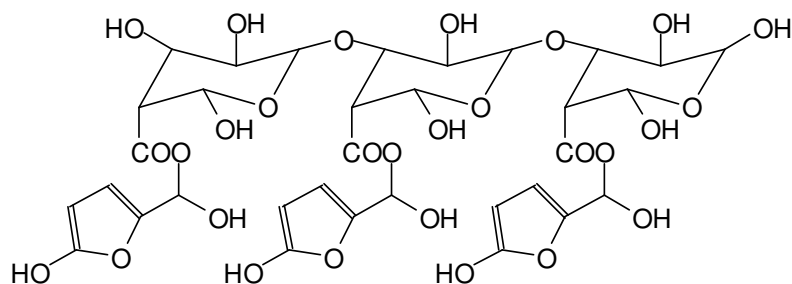


292

293

XVI

294 And species XVII at $882 \text{ MW} + 23 = 905 \text{ Da}$ (Exp. 903 Da) and equally with an $-\text{OH}$
295 substituted by an $-\text{OCH}_3$ thus at 917 Da (with Na^+) (experimental 918 Da) and with two $-\text{OH}$
296 OH groups substituted by $-\text{OCH}_3$ is represented by the peak at 932 Da (Fig. 3e).

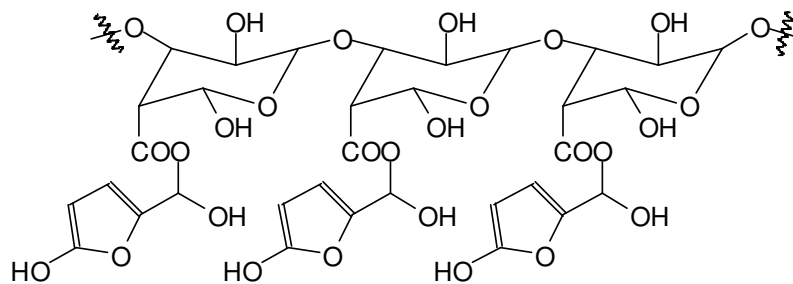


297

298

XVII

299 That presents itself also as a repeating tract of oligomer at $910 \text{ MW}+23 = 933 \text{ Da}$
 300 (experimental and calculated) (Fig. 3e).

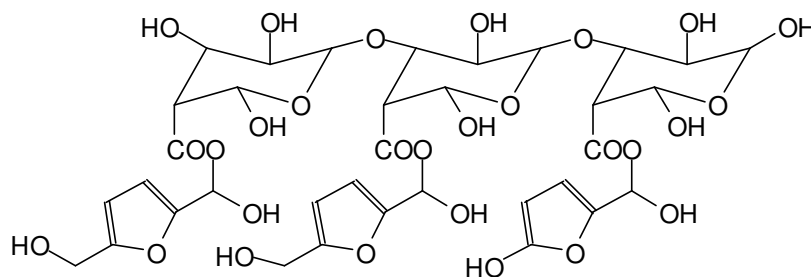


301

302

XVIII

303 As well as species XVIII at $896 \text{ MW}+23 (\text{Na}^+) = 919 \text{ Da}$ (exp 919 Da) as well as species
 304 XIX with two hydroxymethyl furan reactive function at $911 \text{ MW}+23 = 934 \text{ Da}$ exp and
 305 calculated (Fig. 3e).



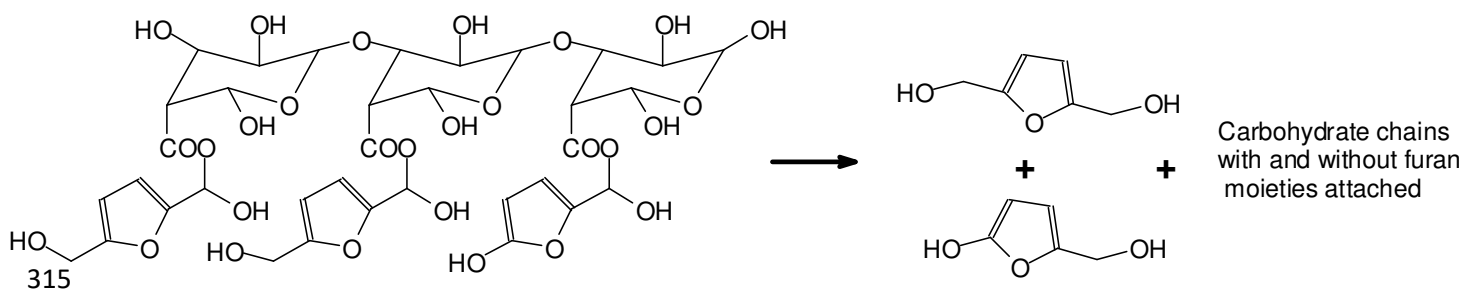
306

307

XIX

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

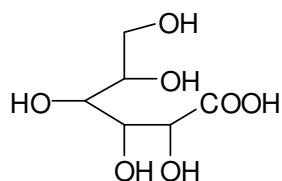
314 The reactions being schematically, for example



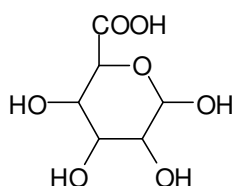
315

316 The oligomer shown above also occurs in Fig. 3e at $882 + 23 (\text{Na}^+) = 905 \text{ Da}$ (903 Da exp)
317 and equally with an $-\text{OH}$ substituted by an $-\text{OCH}_3$ thus at 917 Da (with Na^+) (experimental
318 918 Da) and with two $-\text{OH}$ groups substituted by $-\text{OCH}_3$ is represented by the peak at 932.8
319 Da.

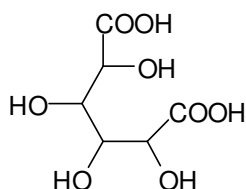
320 In Fig. 3a are also noticeable oxidized hexoses, thus carrying a $-\text{COOH}$ group, such as the
321 one at MW 196 (exp. 198-199Da), and its equivalent $196 + 23 (\text{Na}^+) = 219 \text{ Da}$ (experimental
322 218 Da) and also the unit minus an $-\text{OH} = 180 \text{ Da}$, this being a gluconic acid (Fengel and
323 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 $-\text{OH} = 178 \text{ D}$ as a
326 glucuronic acid repeating unit. It occurs at 193 Da experimental, and 178-179 Da exp.,
327 respectively.



328
329 Equally, Glucaric acid (Fengel and Wegener 1989), MW = 210 Da minus one $-\text{OH} = 194 \text{ Da}$;
330 it occurs at 193 Da (exp). It exists also at $210 + 23 = 233 \text{ Da}$, (exp 233 Da), as shown in Fig.
331 3a.

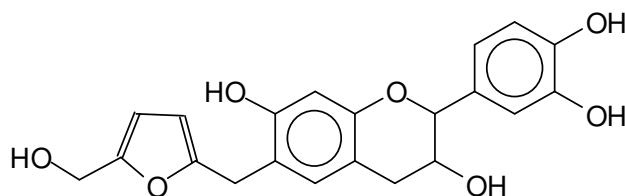


332
333
334 It is of primary interest to also determine if the 5-hydroxy-2-hydroxymethyl furan and the 2,5-
335 dihydroxymethyl furan, obtained by hydrolysis from the sugar oligomers carrying it, are the
336 active hardeners of a tannin-based adhesive. To this purpose MALDI examination of pine
337 tannin hardened by the biosourced *Vachelia nilotica* exudate extract was carried out to

338 determine the structure of the oligomers and of the cross-linking that takes place on
339 hardening.

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

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

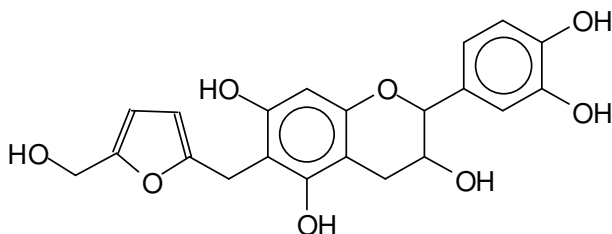


349

350 **XX**

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

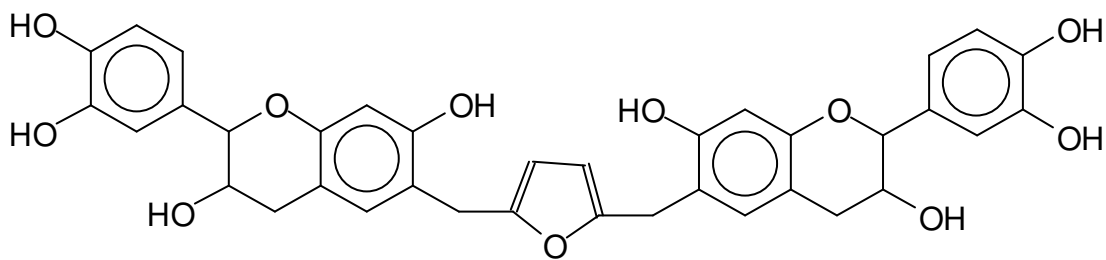
355



356

357 **XXI**

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

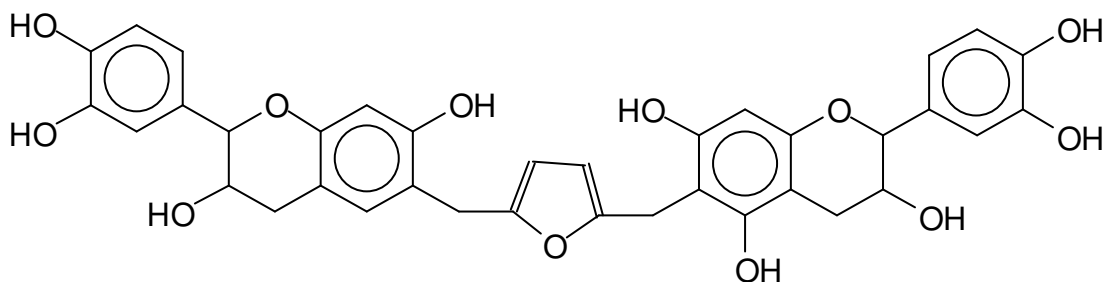


360

361

XXII

362 Structure XXII at 663 Da (with Na⁺) is present (Fig. 4d).

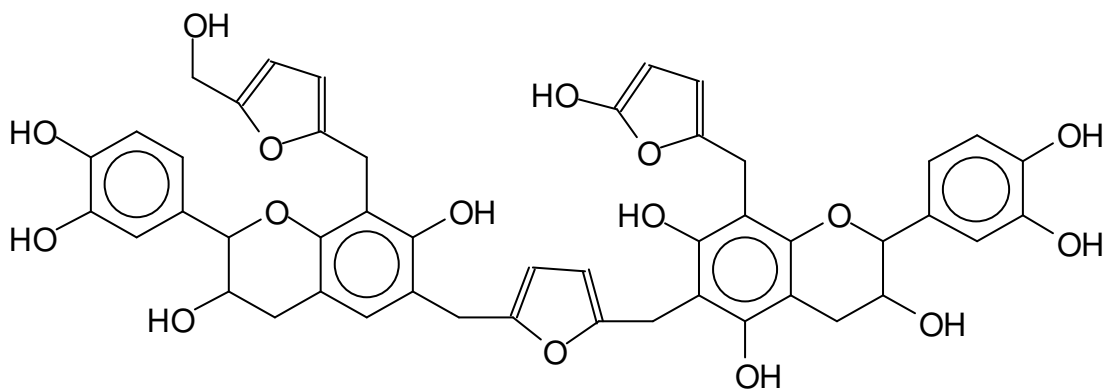


363

364

XXIII

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



366

367

XIV

368 Structure XIV is possibly the one contributing to the peak at 862 Da calculated (exp 859 Da),

369 Fig. 4e. Structures XXII, XXIII, XXIV show that cross-linking has occurred and that 2,5-

370 dihydroxymethyl furan is a rather reactive cross-linker for the pine tannin resin.

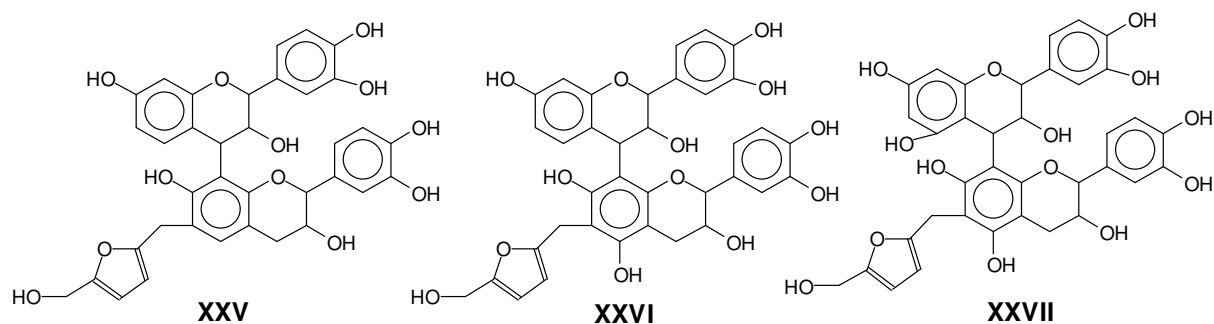
371

372 There are also flavonoid oligomers that have both reacted with 2,5-dihydroxymethyl furan,

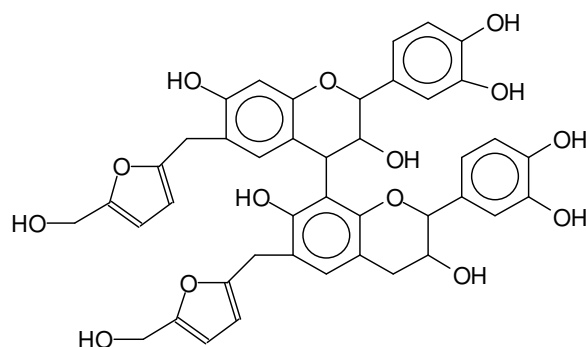
373 such as at 601 Da a dimer of catechin + Na⁺, and at 857 Da a fisetinidin-fisetinidin-catechin

374 trimer +Na⁺ (exp 858 Da).

375 And at 656 Da without Na⁺, calculated and experimental, it is found a fisetinidin dimer having
376 reacted with one 2,5-dihydroxymethyl furan and of structure XXV, with at 695 Da (with Na⁺)
377 (exp. 697) a fisetinidin-catechin dimer reacted with one 2,5-dihydroxymethyl furan and of
378 structure XXVI, and at 711 Da (with Na⁺) (exp 711-713) an equally reacted catechin dimer of
379 structure XXVII (Fig. 4d,e).

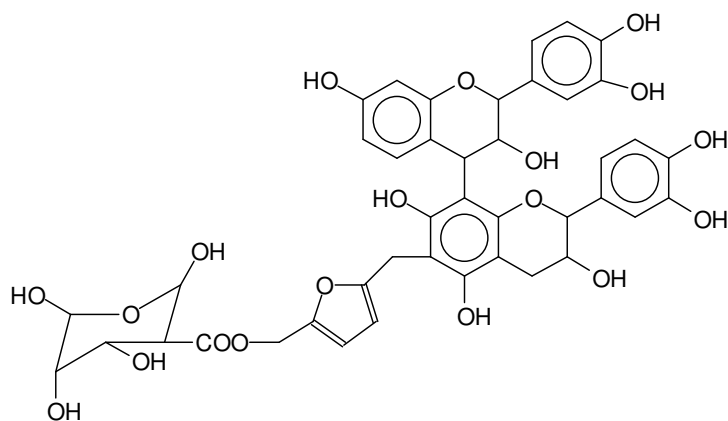


381 Equally, flavonoid dimers reacted with 2 molecules of 2,5-dihydroxymethyl furan are also
382 present. For example, the peak at 789 Da (with Na⁺) (exp 787 Da) (Fig. 4d,e) could
383 corresponds a structure of the type



385

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



XXIX

389

390

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

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

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

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

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

433

434 CONCLUSIONS

435 Totally “bio” wood particleboard panels have been prepared with a totally “bio” adhesive
436 using as hardener of a maritime pine tannin adhesive the extract of exudates of the African
437 trees *Vachellia nilotica* and *Senegalia senegal*. The analysis of these showed that the reactive
438 species of these hardeners were furan hydroxymethyl species linked to carbohydrate
439 oligomers. These gave 2-hydroxy-5-hydroxymethyl furan and especially 2,5-dihydroxymethyl
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
443 binder. The gel times were slower than what obtainable with paraformaldehyde but
444 sufficiently fast to possibly be of industrial significance.

445

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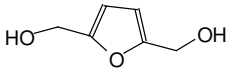
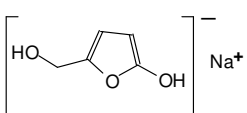
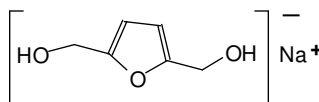
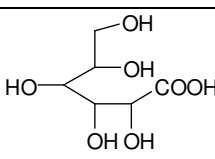
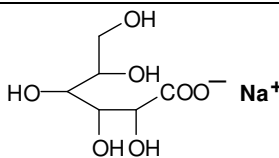
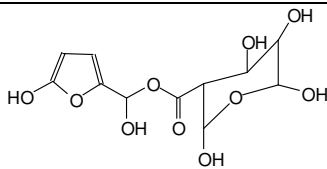
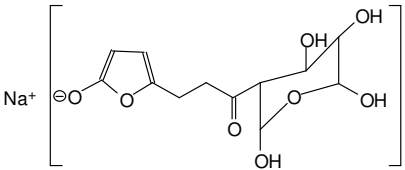
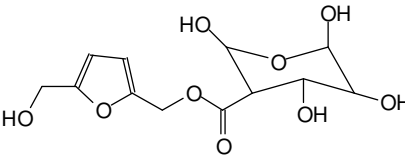
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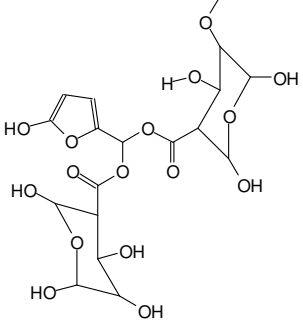
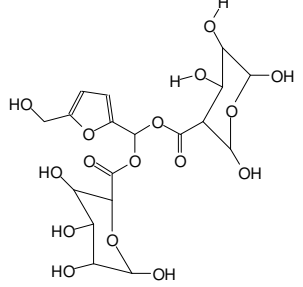
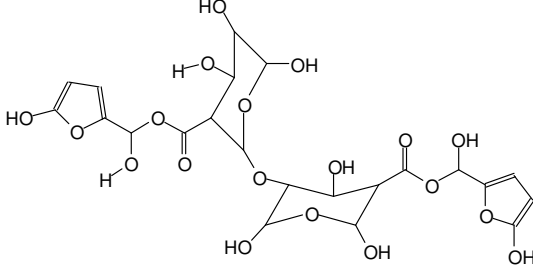
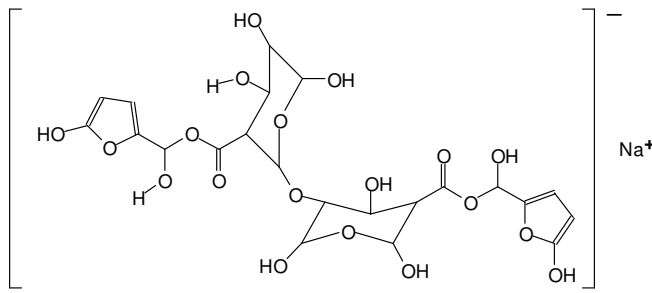
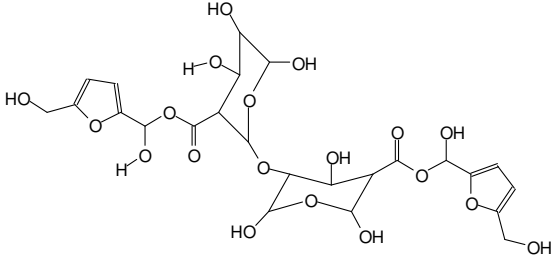
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564 laminated composite based on tannin resin. *J. Adhesion* 93, 461-467.

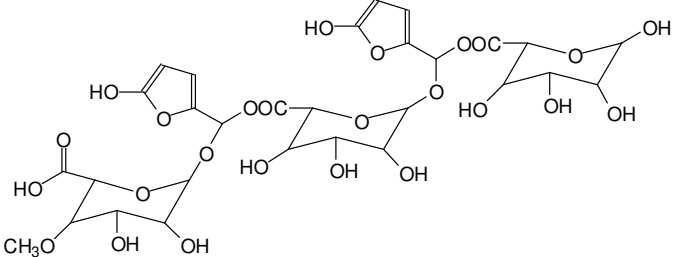
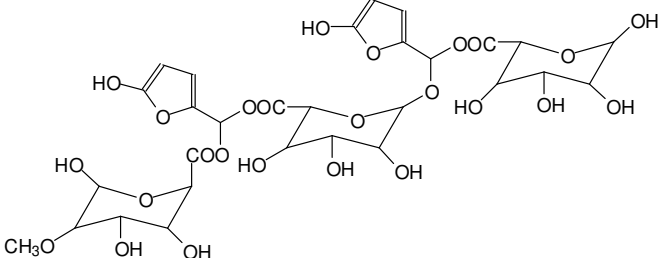
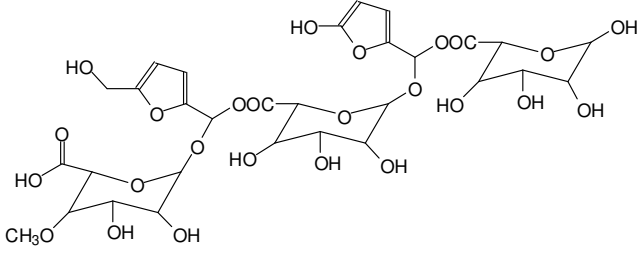
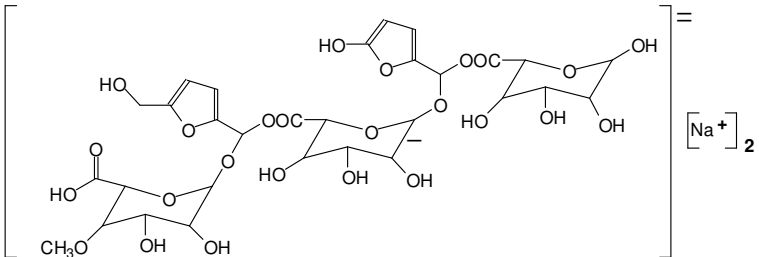
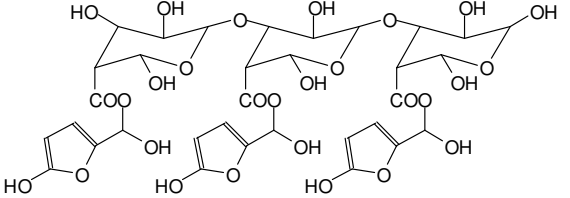
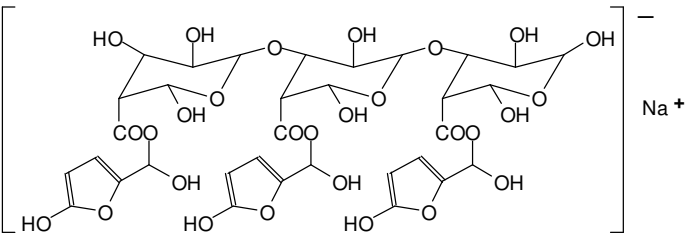
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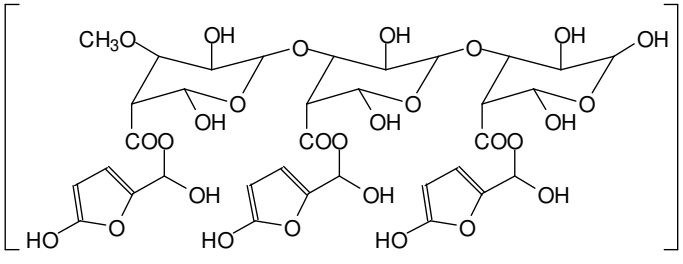
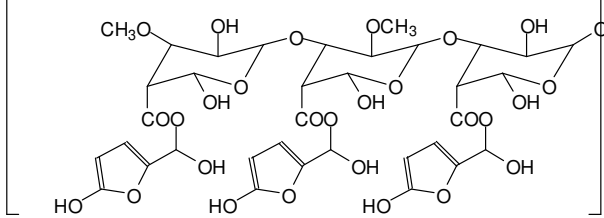
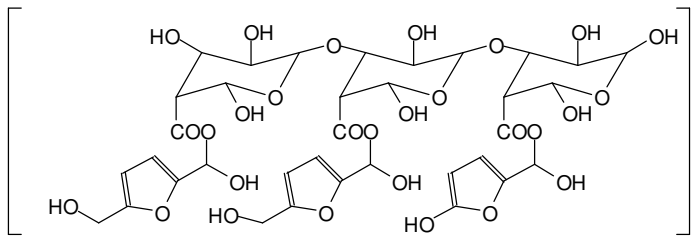
566 **Acknowledgements:** The LERMAB of the University of Lorraine is supported by a grant
567 overseen by the French National Research Agency(ANR) as part of the Laboratory of
568 Excellence (Labex) ARBRE.

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

128 Da	
138-139 Da	
150-151 Da	
178-179 Da	Gluconic and glucuronic acid repeating units
193-194 Da	Glucuronic acid
198-199 Da	
219 Da	
233 Da	Glucaric acid + Na ⁺
304-305 Da	
313 Da	
326- 327 Da	

495-496 Da	
495-496 Da	
594 Da	
617 Da	
619 Da	

785-786 Da	
785-786 Da	
799-801 Da	
845-847 Da	
882 Da	
903-905 Da	

917-918 Da	
932 Da	
933 Da	

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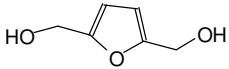
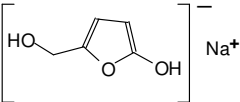
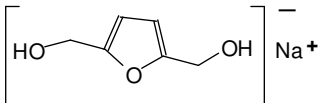
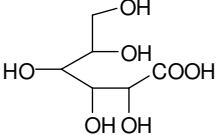
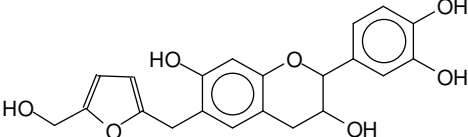
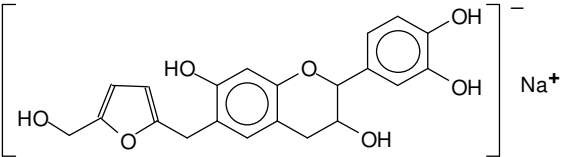
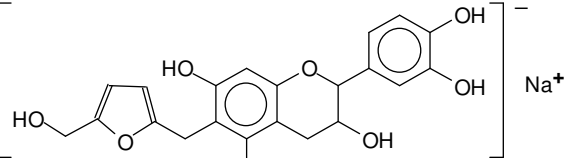
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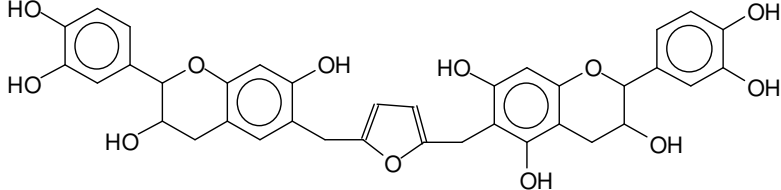
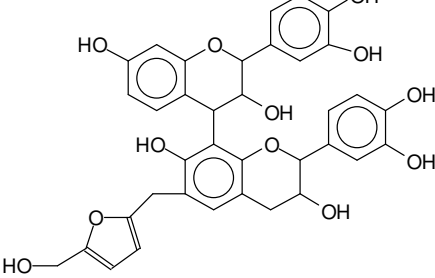
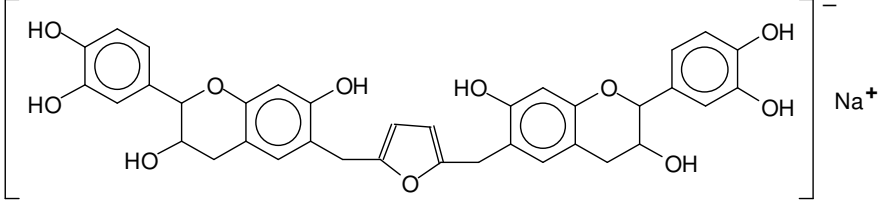
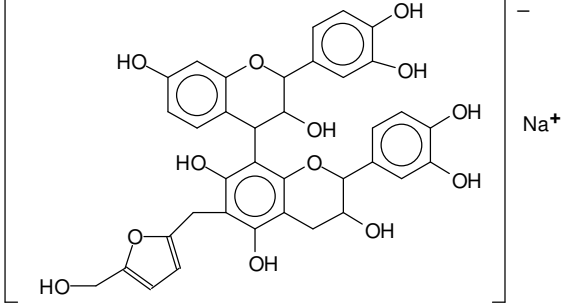
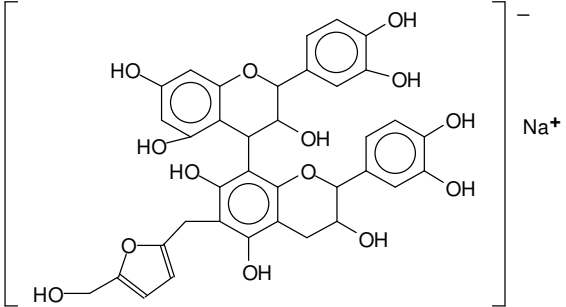
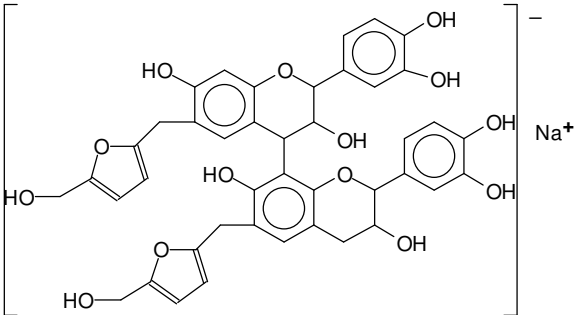
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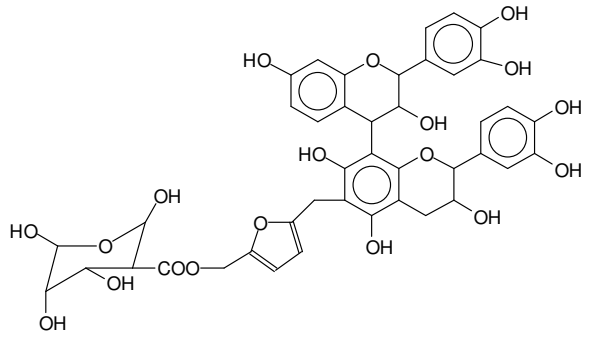
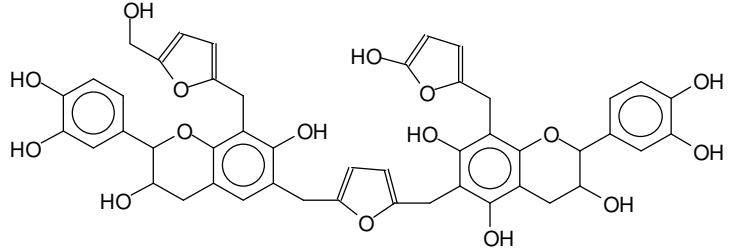
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589 Table 2. MALDI ToF peaks. Oligomers structures assignments for the reaction of the
 590 exudates with a flavonoid tannin (Fig. 4).

128 Da	
138-139 Da	
150-151 Da	
178-179 Da	Gluconic and glucuronic acid repeating units
198-199 Da	
273 Da	Fisetinidin monomer
294-295 Da	Fisetinidin monomer + Na ⁺
290 Da	Catechin and epicatechin monomers
304 Da	Gallocatechin (delphinidin) monomer
327 Da	Gallocatechin (delphinidin) monomer ^o Na ⁺
385 Da	
406 Da	
420-422 Da	
601 Da	Catechin dimer + Na ⁺

655 Da	
656 Da	
663 Da	
695-697 Da	
711-713 Da	
787 Da	

847 Da	
858 Da	Fisetinidin-Fidetinidin-Catechin trimer +Na+
862 Da	

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594 Table 3. Internal Bond (IB) strength results of particleboard bonded with pure maritime pine
595 bark tannin hardened with the exudate of *Vachellia nilotica* and with a urea-formaldehyde
596 (UF) control. The results shown are the average of 3 panels each with 5 specimens tested for
597 each panel.

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599 Resin	Panel	Moisture content	Dry IB Strength (MPa)
600 type	density (kg/m ³)	after pressing (%)	
602 Experimental	670 \pm 9	9.8	0.64 \pm 0.05
603 UF control	682 \pm 12	10,4	0.72 \pm 0.02
604 EN319 requirements	-	-	\geq 0.35

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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 ^{13}C NMR of (a) the exudate extract of *Vachellia nilotica*, 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.

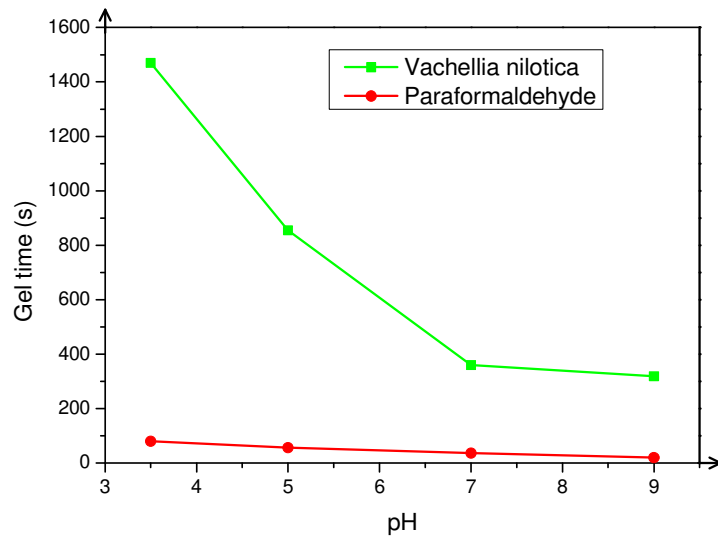
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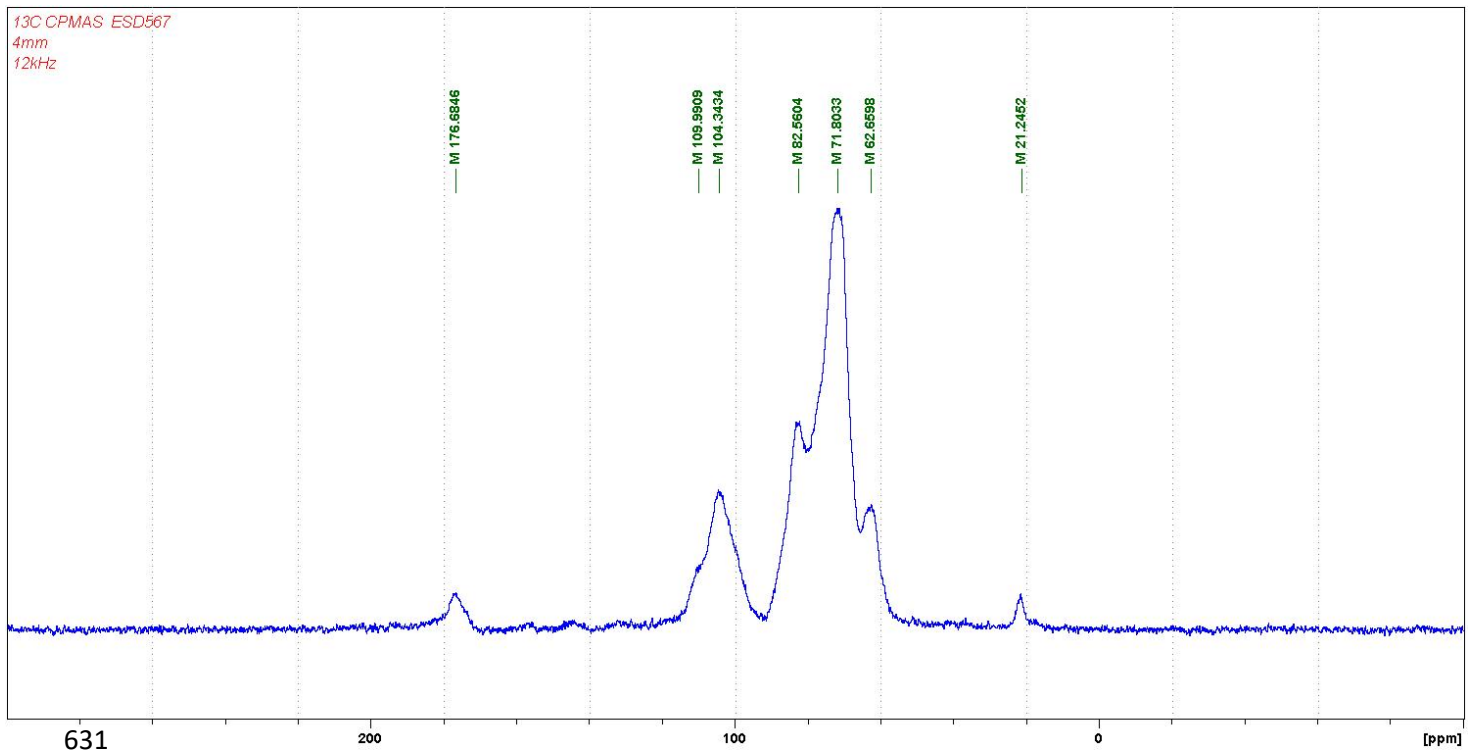
627



628 Figure 1

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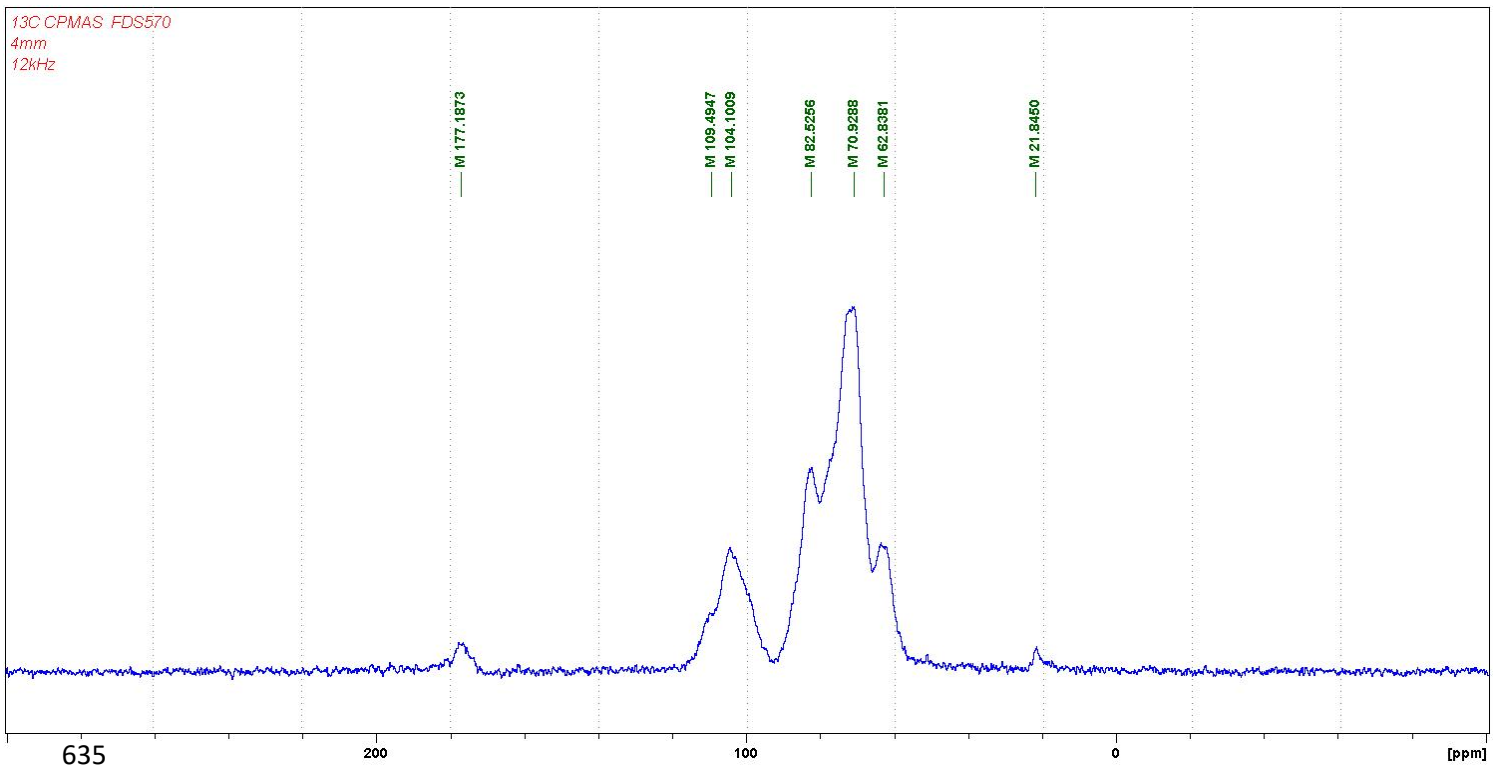
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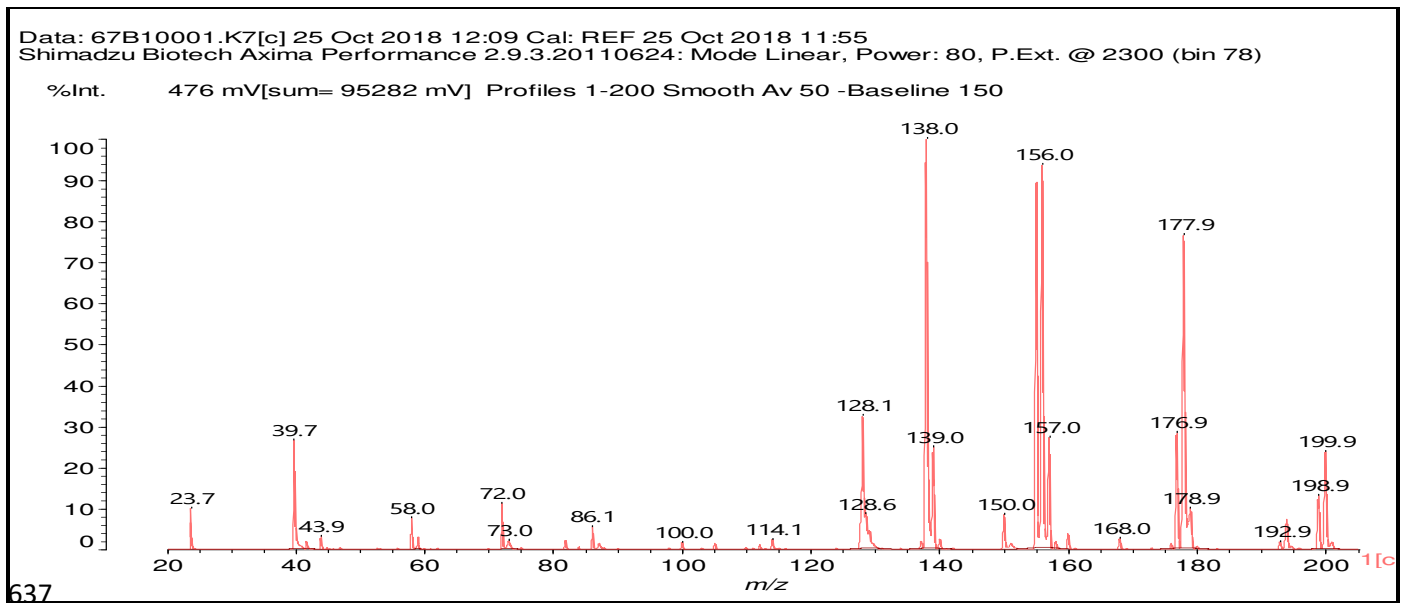
632 Figure 2a.

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636 Fig. 2b.

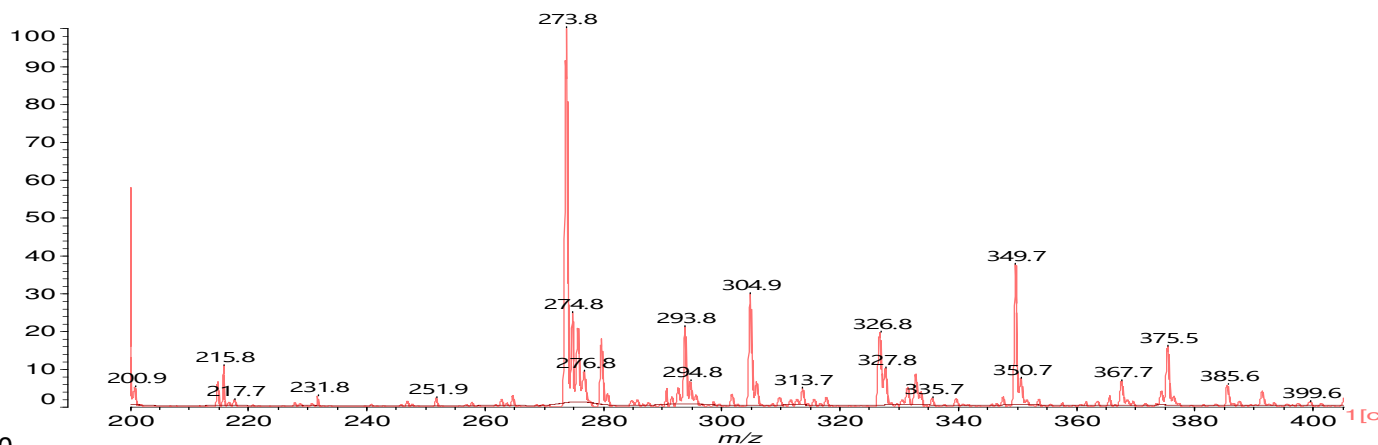


638 Fig. 3a

639

Data: 67B10001.K7[c] 25 Oct 2018 12:09 Cal: REF 25 Oct 2018 11:55
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 80, P.Ext. @ 2300 (bin 78)

%Int. 170 mV[sum= 33964 mV] Profiles 1-200 Smooth Av 50 -Baseline 150

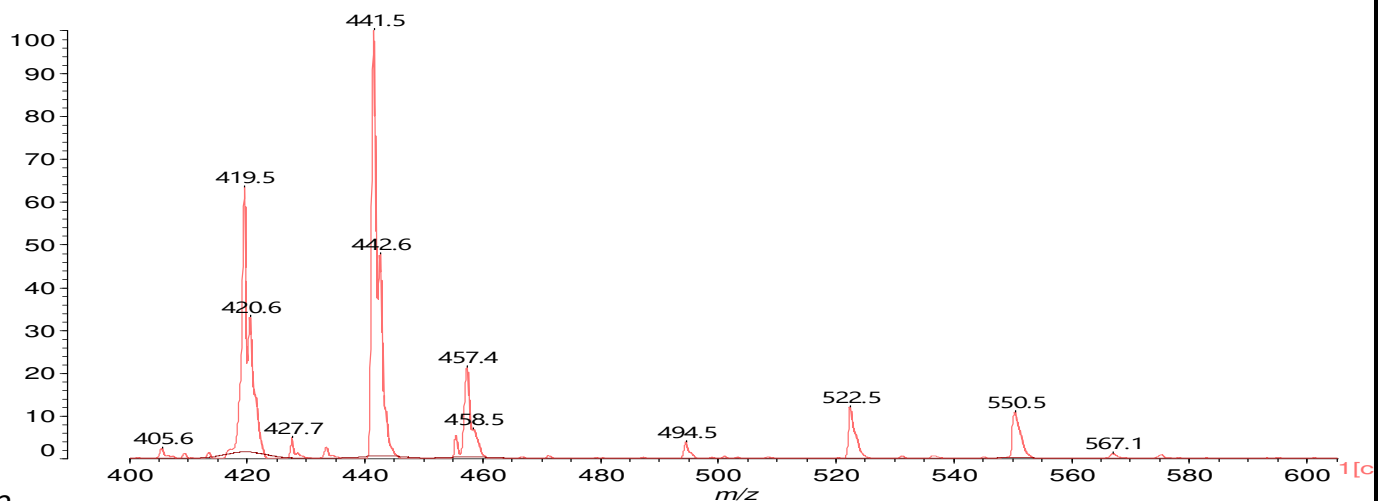


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641 Fig. 3b

Data: 67B10001.K7[c] 25 Oct 2018 12:09 Cal: REF 25 Oct 2018 11:55
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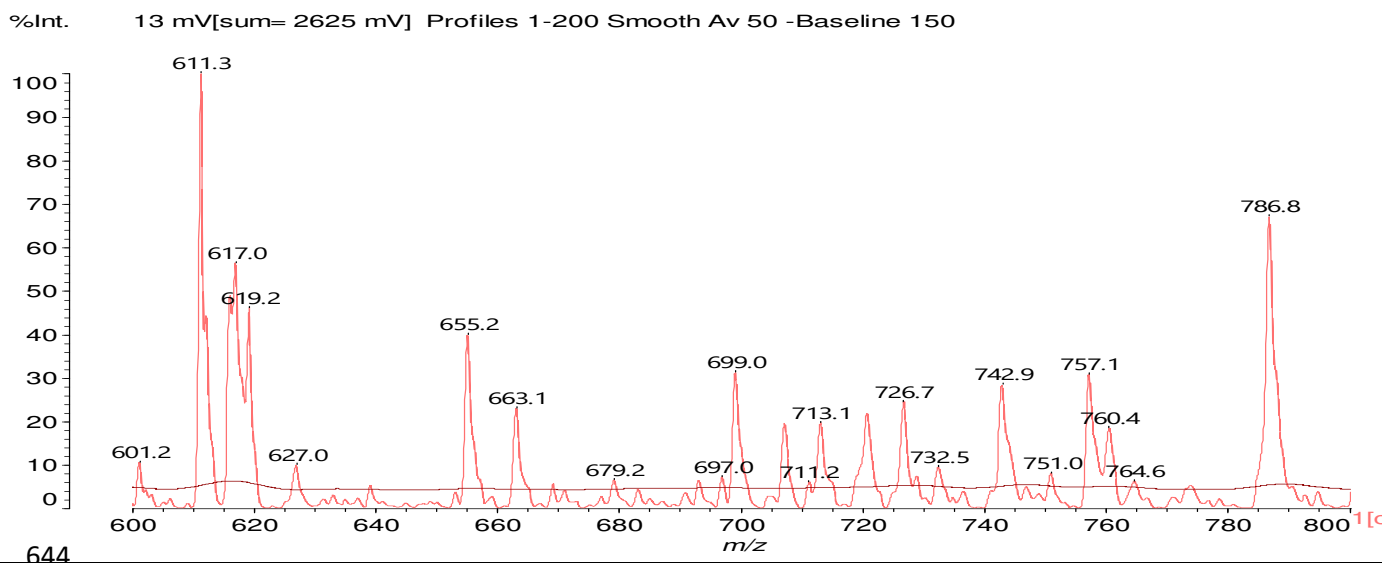
%Int. 519 mV[sum= 103801 mV] Profiles 1-200 Smooth Av 50 -Baseline 150



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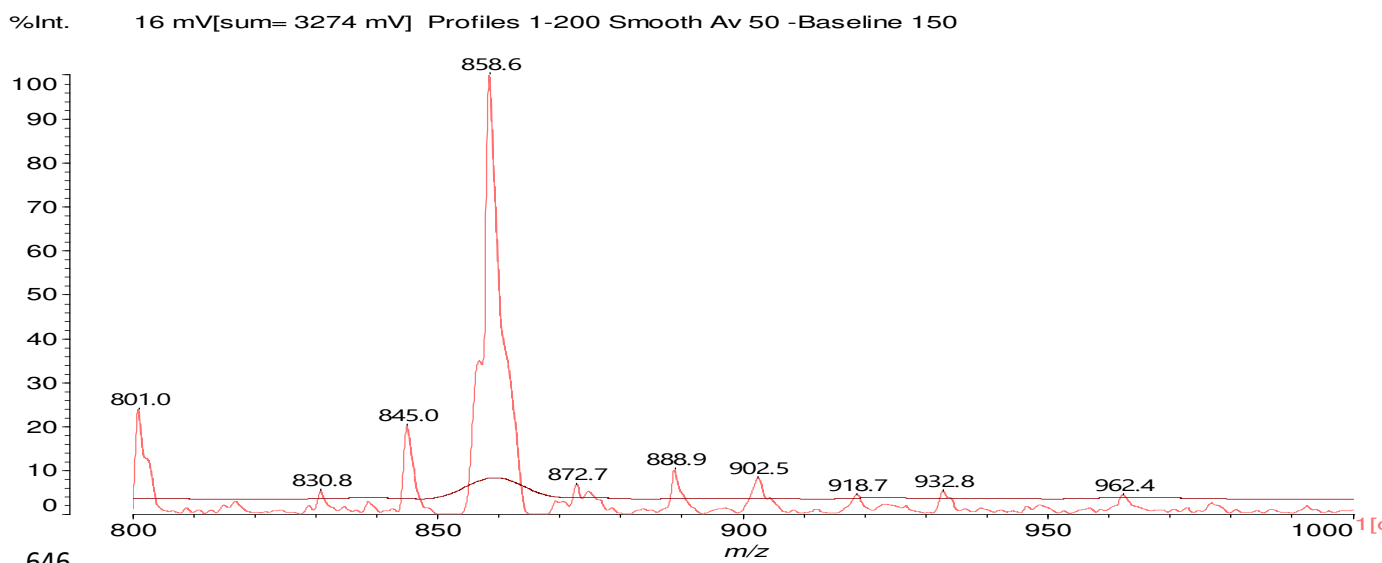
643 Fig. 3c

Data: 67B10001.K7[c] 25 Oct 2018 12:09 Cal: REF 25 Oct 2018 11:55
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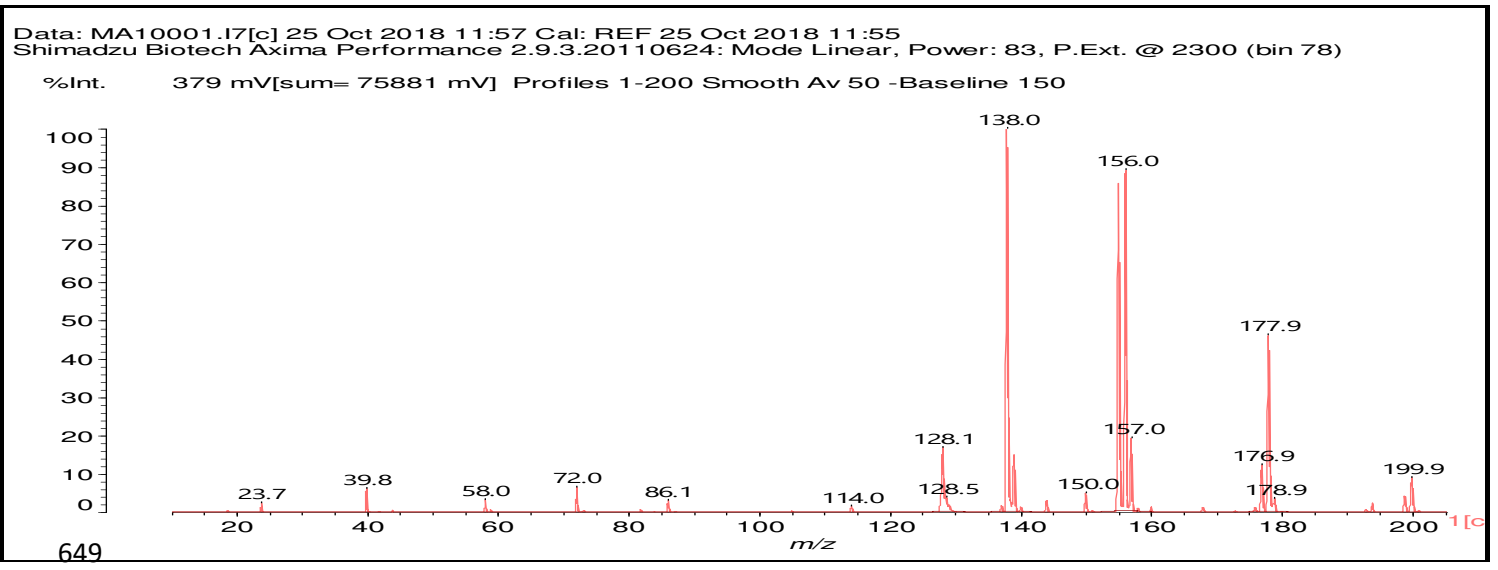
645 Fig. 3d

Data: 67B10001.K7[c] 25 Oct 2018 12:09 Cal: REF 25 Oct 2018 11:55
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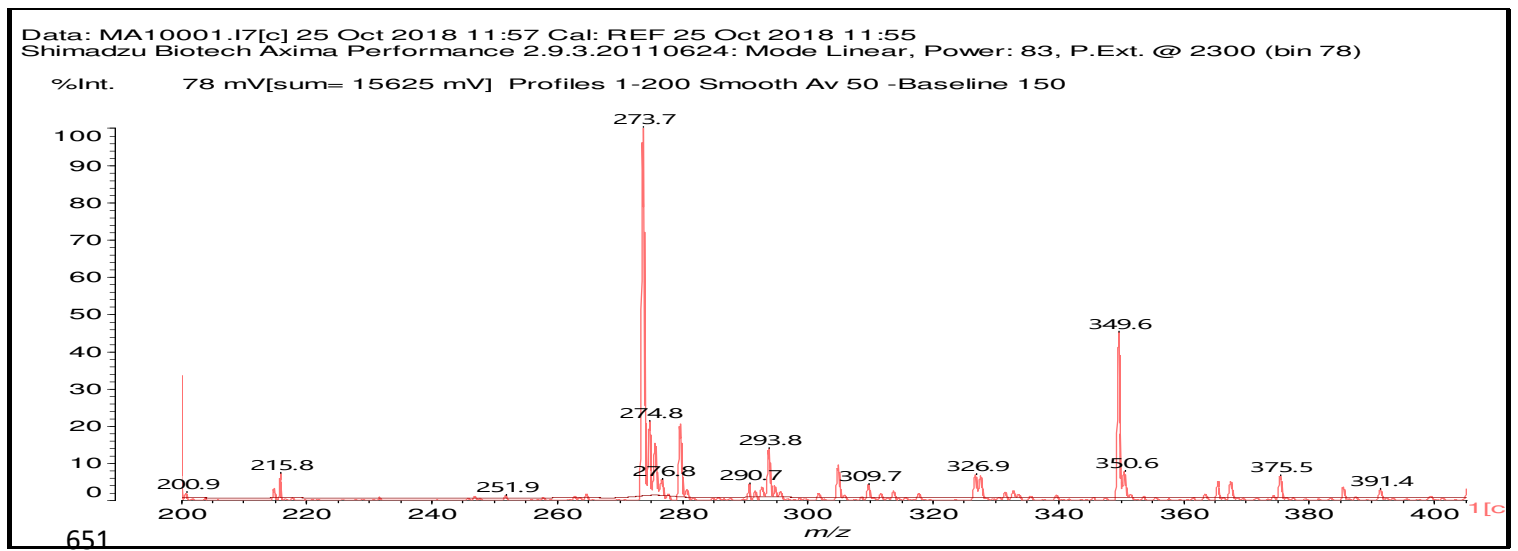


647 Fig. 3e

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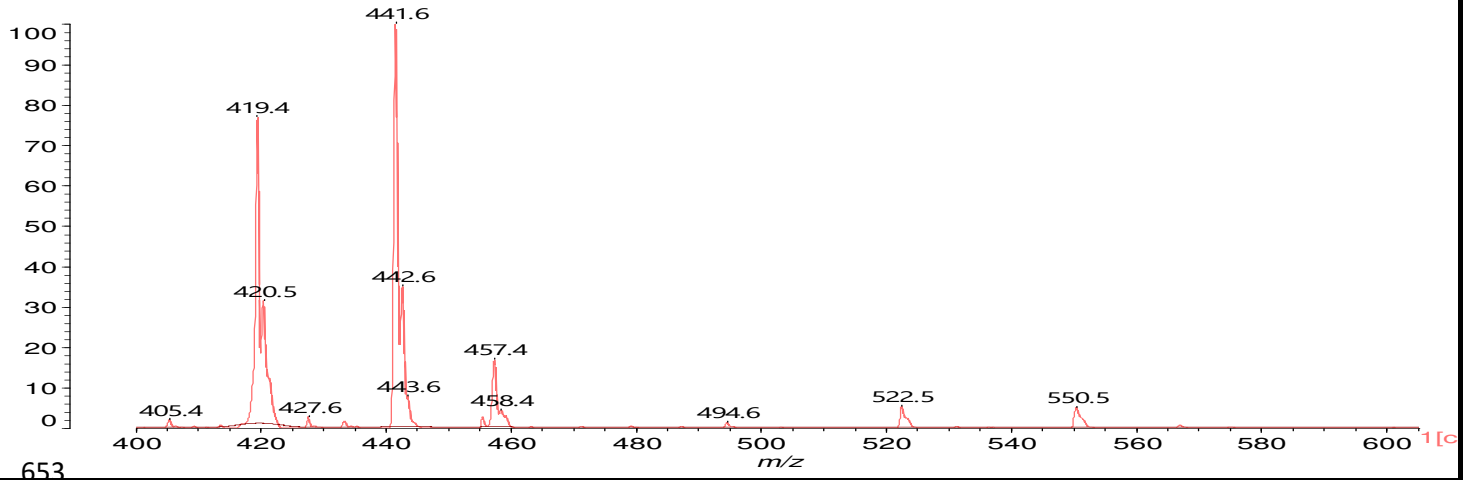
650 Fig. 4a



652 Fig. 4b.

Data: MA10001.I7[c] 25 Oct 2018 11:57 Cal: REF 25 Oct 2018 11:55
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 83, P.Ext. @ 2300 (bin 78)

%Int. 242 mV[sum= 48471 mV] Profiles 1-200 Smooth Av 50 -Baseline 150

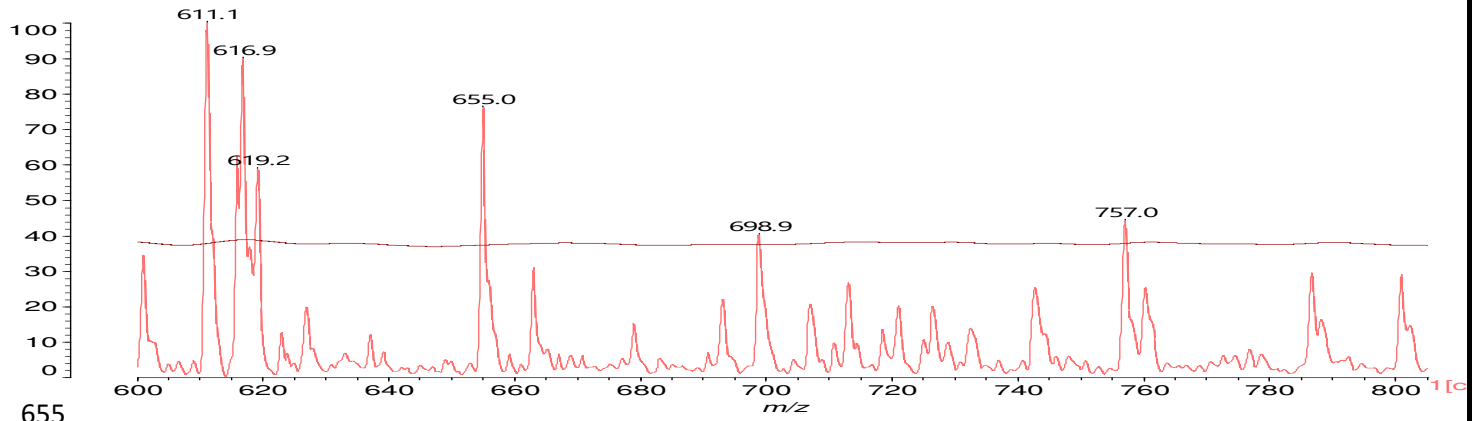


653

654 Up Fig 4c, Down Fig. 4d

Data: MA10001.I7[c] 25 Oct 2018 11:57 Cal: REF 25 Oct 2018 11:55
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 83, P.Ext. @ 2300 (bin 78)

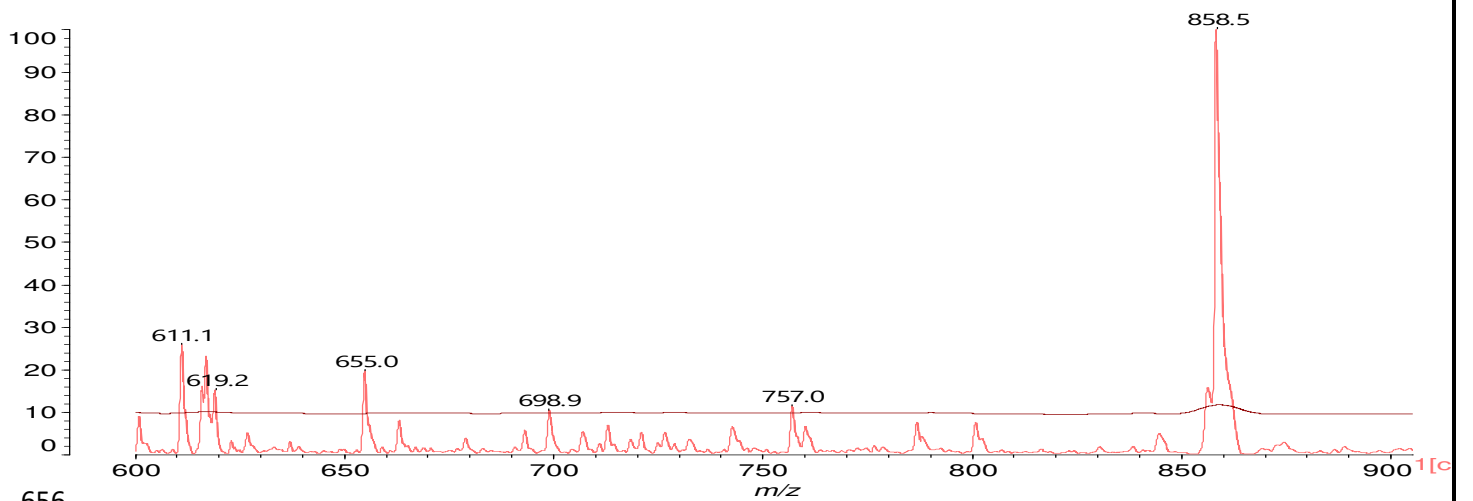
%Int. 1.4 mV[sum= 283 mV] Profiles 1-200 Smooth Av 50 -Baseline 150



655

Data: MA10001.I7[c] 25 Oct 2018 11:57 Cal: REF 25 Oct 2018 11:55
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 83, P.Ext. @ 2300 (bin 78)

%Int. 5.5 mV[sum= 1096 mV] Profiles 1-200 Smooth Av 50 -Baseline 150

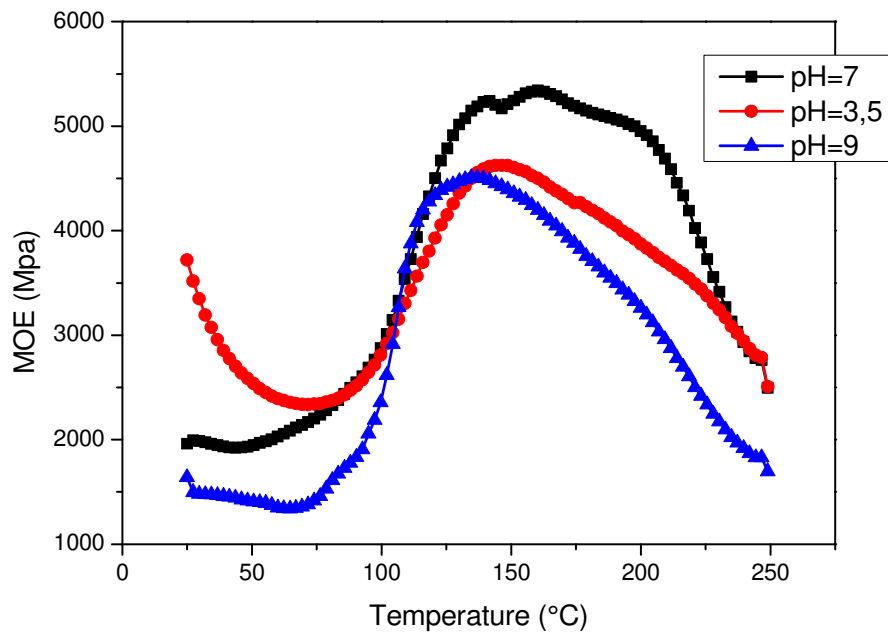


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657 Fig. 4e

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Fig. 5