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1 **Extraction of acetylated glucuronoxylans and glucomannans from**
2 **Okoume (*Aucoumea klaineana* Pierre) sapwood and heartwood by**
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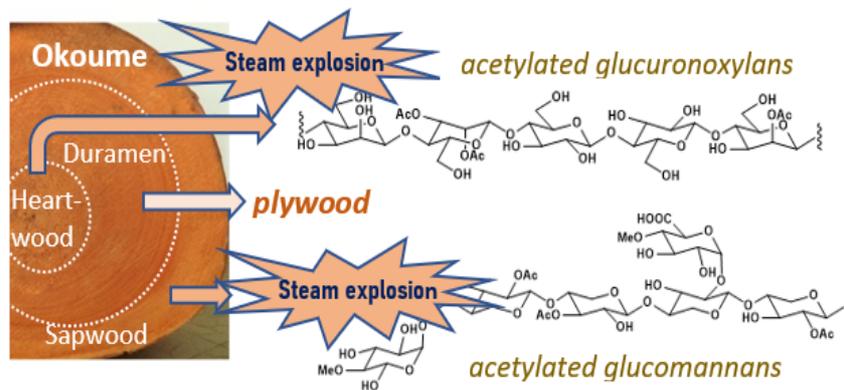
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14
15

16 **Abstract**

17 *Aucoumea klaineana* Pierre (okoume) is a tropical hardwood of industrial importance, used
18 for veneers and plywood production. Various conditions of Steam Explosion (SE) treatment
19 (temperature, residence time, pH) have been applied on okoume co-products, sapwood
20 (SW) and heartwood (HW) for the extraction of polymeric hemicelluloses. Conventional
21 extractions with alkali or dimethyl sulfoxide (DMSO) were also performed from delignified
22 SW and HW for comparison. The hemicelluloses extracts have been characterized by HSQC-
23 NMR, FTIR, size exclusion chromatography. The acetyl contents have been determined by
24 HPLC after saponification and from HSQC spectra. Using basic impregnation prior to SE
25 (NaOH-SE), high molecular mass glucuronoxylans (GX, Mw = 65-100 KDa) were recovered in
26 3-6 % yields. A neutral impregnation (H₂O-SE) produced O2 and/or O3 acetylated GX and
27 glucomannans (GM), preserving the acetyl moieties in a greater extent compared to the mild
28 DMSO extraction (% Ac ≈ 6.6-8.4% and 1.0-4.1 % w/w respectively). This study provides
29 insights on the composition of SW and HW okoume with a view to further innovative
30 processing and valorization including the preparation of films with advanced properties for
31 food packaging.

32 **Key words:** *Aucoumea klaineana* Pierre; steam explosion; acetylated glucomannans;
33 acetylated glucuronoxylans; sapwood; heartwood

34 1. Introduction

35
36 The economic viability of the biorefineries depends of the optimal valorization of plant
37 resources including the utilization of non-cellulosic constituents. Hemicelluloses are among
38 the main components of wood and constitute a vast, heterogeneous and complex family of
39 polysaccharides, containing diverse sugars and uronic acids (Ishii et al., 2001, Chadni et al.,
40 2019). Hardwood hemicellulosic fraction is mainly composed of glucuronoxylans (\approx 15-30%
41 of wood) which have a backbone of β - 1,4-linked xylose residues substituted with α -linked 4-
42 *O*-Me- β -*D*-glucopyranosyl uronic acid on *O*-2 of xylosyl residue. Hardwood can also contain a
43 minor amount of glucomannans (\approx 4% of wood) which have a backbone of β -1,4-linked
44 glucopyranosyl / mannopyranosyl units in a linear or slightly branched chain. These
45 polysaccharides are usually diversely acetylated on the sugar backbone (Willfor et al. 2005).
46 Unlike cellulose, which has been used industrially for a very long time, applications involving
47 polymeric hemicelluloses are rare and the potential of hemicelluloses is still very little
48 exploited. However, due to their chemical structure and high molar masses, hemicelluloses
49 can be used to produce promising materials for various applications. One of the most
50 studied applications for polymeric hemicelluloses is the design of films with advanced
51 properties (e.g. biodegradability, edibility, barrier effect) for food packaging (Chadni et al.,
52 2020, Zhao et al., 2020).

53 Various processes have been proposed for the recovery of hemicellulosic polymers from
54 lignocellulosic matrix including alkali extraction of xylans and/or glucuronoxylans from
55 agricultural co-products and liquid hot water extraction (Zhao et al. 2020). It has also been
56 reported that galactoglucomannans can be recovered from the water stream of
57 thermomechanical pulping of softwood using membrane technologies (Kishani et al., 2018,
58 Willfor et al, 2003). The recovery of acetylated hemicelluloses could be of great interest for
59 biological and material applications since acetylation degree affects the accessibility of
60 polysaccharides to microbes, their solubility in water (Michalak et al. 2018, Voepel et al.
61 2009) and the physico-chemical properties of hemicelluloses-based materials (e.g. barrier
62 properties of films, Kishani et al., 2018).

63 However, the recovery of acetylated and high molecular mass hemicelluloses from wood
64 with a minimum of degradation is still challenging. In fact, the currently applied methods
65 usually rely on partly modified and deacetylated polysaccharides. For characterization

66 purpose slightly modified and acetylated hemicelluloses can be recovered from
67 holocellulose by DMSO extraction (Evtuguin et al. 2003, Marques et al. 2010).
68 Steam explosion (SE) is one of the most promising processes for biomass fractionation and
69 pretreatment. SE is a thermo-mechanico-chemical treatment involving a steaming step
70 followed by an explosive decompression provoking a partial breakdown of the lignocellulosic
71 complex (Espirito Santo et al., 2020, Marques et al., 2020, Inseemeeesak and Areeprasert,
72 2020). This process is commonly used for increasing the accessibility of cellulose to
73 enzymatic hydrolysis and has been developed, even at commercial stage, for cellulosic
74 bioethanol production. More marginally, SE has also been described for high molecular mass
75 hemicelluloses extraction from lignocellulosic biomass. Compared to a hot water extraction,
76 it has been demonstrated by Wojtasz-Mucha et al. (2017) that SE provoked a more effective
77 hemicelluloses extraction due to the advective mass transport during the pressure release
78 step (explosion). Krawczyk et al. (2008) reported the isolation of arabinoxylans from barley
79 husks by SE after water impregnation and ultra-filtration. In our group, we studied the
80 extraction of arabinoxylans and galactoglucomannans from spruce by SE (Chadni et al., 2019,
81 2020). Extraction selectivity as a function of the pH of the SE treatment was demonstrated:
82 for a basic impregnation arabinoglucuronoglycans were recovered in relatively high yields
83 whereas for water impregnation highly acetylated galactoglucomannans were isolated. It
84 was concluded that SE could constitute an effective technique for the recovery of slightly
85 modified and acetylated hemicelluloses from wood of application interest (e.g. food
86 packaging).

87 *Aucoumea klaineana* Pierre (okoume) is a fast-growing hardwood species of great industrial
88 importance in Central-Africa. Okoume is primarily used for veneers and plywood production.
89 In Gabon, the okoume wood industry produces approximately $1.5 \cdot 10^6 \text{ m}^3$ of transformed
90 wood and $750\,000 \text{ m}^3$ of waste per year currently not properly used. In wood stem,
91 heartwood (HW) is the inner part characterized by its high mechanical properties and
92 sapwood (SP) the outer part with a higher porosity and moisture content. Due to these
93 properties, okoume SW and HW have been considered as low value coproducts, excluded
94 from industrial transformation such as trenching, veneers and plywood production (Ngwa
95 Obame et al., 2019). There are relatively few publications concerning the comparison
96 between sapwood (SW)/heartwood (HW) composition. Unlike HW, SW is comprised of living
97 cells and allows the water transport and nutrients storage, characterized by a higher

98 porosity and permeability. Willford et al. reported in 2005 the amount and composition of
99 sugars in SW and HW of 11 industrially important hardwood species from temperate areas
100 (Willford et al. 2005). More recently, extractives content of bark, SW and HW of okoume were
101 described (Engozogho et al., 2015) but to the best of our knowledge, the sugars composition
102 of SW /HW of tropical species has never been investigated. However, in a context of an
103 optimal valorization of bioresources, a better knowledge of the chemical composition of the
104 different parts of industrial wood, including co-products, is needed.

105 In previous papers, we have described organosolv and SE pretreatment of okoume SW under
106 various conditions for lignin extraction and characterization but also for ethanol production
107 (Ngwa Obame et al., 2019, Safou-Tchiama et al. 2016). The goal and the novelty of the
108 present work are twofold: (1) to analyze the hemicelluloses composition of HW and SW of a
109 tropical hardwood species and (2) to study the recovery of polymeric hemicelluloses from
110 hardwood during SE pretreatment for further utilizations. A detailed characterization of
111 acetylated hemicelluloses was carried out by NMR and chromatographic methods in order to
112 better understand the parameters impacting the structure of the extracted polysaccharides,
113 to anticipate their future applications and facilitating further processing.

114

115 2. Material and methods

116 2.1. Raw material

117 The samples used in this study were collected from an Okoume (*Aucoumea klaineana Pierre*)
118 log in the Nzamaligué natural forest of Gabon by the “Société Equatoriale d'Exploitation
119 Forestière SEEF”. The Okoume SW comes from slab waste, while the internal HW from the
120 peeling core co-products.

121 2.2. Conventional hemicelluloses extraction with NaOH and DMSO

122 Sawdust from Okoume HW and SW (< 0.16 mm) was Soxhlet extracted using toluene /
123 ethanol / methanol (4:1:1 v/v/v) (Safou-Tchiama et al. 2017). The extracted sawdust was
124 dried at 105°C and stored in a plastic bag at room temperature before use. Extract-free
125 sawdust was depectinized with a 1% (w/w) of ammonium oxalate solution (2 h at 80°C) and
126 then dried at 40°C. Delignification was carried out in a water bath under reflux at 70°C by
127 dispersing 1.5 g of depectinized sawdust in 125 mL of deionized water. Subsequently, 1 g of
128 sodium chlorite and 1 mL of glacial acetic acid were added every 2 h until complete
129 bleaching of the biomass. The delignified residue was carefully washed with deionized water

130 and filtered under vacuum. The white fibrous solid residue (holocellulose) was collected and
131 dried at 40 °C. Alkaline extraction was carried out under magnetic stirring at 70 °C with 1 g of
132 dry holocellulose in 50 mL of 2% (w/w) of NaOH. After 2 hrs, the liquid phase was recovered.
133 The residue was extracted again with 50 mL of 2% NaOH for 2 hrs. Both liquid phases were
134 acidified with 20% (w/w) of acetic acid to a pH between 5.5 and 6. The hemicelluloses
135 precipitated by the addition of 3 volumes of ethanol were recovered by centrifugation at
136 4000 rpm for 10 min at room temperature. The recovered hemicelluloses were dried at 40°C
137 and stored in plastic jars before analysis. The hemicelluloses yields were calculated as mass
138 percentage of dry wood. The DMSO extraction of hemicelluloses was performed on
139 holocellulose (1:25 solid/liquid) under magnetic stirring for 15 hrs at 70°C. Three volumes of
140 ethanol were added. The hemicelluloses were recovered by centrifugation at 4000 rpm for
141 10 min and drying at 40°C. Yields of hemicelluloses were calculated as mass percentage of
142 dry wood.

143 **2.3. Extraction of hemicelluloses by steam explosion**

144 Extraction of hemicelluloses by SE has been carried out by adapting the protocol described
145 by Chadni et al. 2019 Sawdust from Okoume HW and SW of about 2 mm size was first dried
146 at 105 °C overnight. Then 50 g of biomass were impregnated for 15 hrs in 1 M aqueous
147 NaOH (solid/liquid ratio 1:7, NaOH-SE) or in water (solid/liquid ratio 1:7, H₂O-SE) before SE
148 (Fig. 1).

149 The impregnated sawdust was then filtered and placed directly into a 2 L SE reactor. The
150 sawdust was treated by injection of saturated steam at various temperatures and residence
151 times (see Table 1), then a pneumatic ball valve was opened to abruptly drop the pressure
152 and transport the biomass to the explosion chamber. The steam explosions were set at
153 temperatures between 170 °C and 210°C and a residence time of 5 min to 10 min. The
154 severity factor for each experiment was calculated by correlating temperature and retention
155 time using the following equation (Overend and Chornet, 1987):

Eq. 1

$$S = \log \left[t_s \cdot \exp \left(\frac{T - 100}{14.75} \right) \right]$$

156

t_s is the residence time (min) and T is the temperature (°C).

157 After SE pre-treatment, the hemicelluloses-rich liquid fraction was separated from the
158 treated wood by filtration. For NaOH-SE, the pH was adjusted between 5.5 and 6 with H₂SO₄
159 72% (w/v). The liquid fraction was concentrated using a rotary evaporator until a volume of

160 \approx 100 mL. The hemicelluloses were precipitated with 4 volumes of ethanol, then separated
161 by centrifugation at 40,000 rpm for 10 min. The supernatant was gently removed and the
162 solid (composed of polymeric hemicelluloses) was retained for the dialysis step. The dialysis
163 was performed for 3 days by filling a dialysis tube (cut-off of 2.5 kDa) with the hemicelluloses
164 solubilized in ultrapure water. Finally, the dialysate consisting of hemicelluloses was freeze-
165 dried.

166 **Fig.1**

167 **2.4. Measurement of monosaccharides and uronic acids by HPEAC-PAD**

168 The processing and analysis of the chemical composition of the extracts was performed
169 using the National Renewable Energy Laboratory (NREL/TP-510-42618) standard.
170 Monosaccharide and uronic acid concentrations were quantified by high performance anion
171 exchange chromatography coupled with a pulsed amperometric detector (HPEAC-PAD:
172 Dionex ICS-3000). The separation was carried out on a CarboPac PA20 (Dionex) column at a
173 temperature of 35 °C and with an isocratic eluent flow rate of 0.4 mL.min⁻¹, with the
174 following composition: 99.2% ultrapure water / 0.8% of 250 mM NaOH (0–20 min) ; 75%
175 ultrapure water / 20% of 250 mM NaOH / 5% 1 M of CH₃COONa - 20 mM NaOH (20–37 min)
176 and 40% of ultrapure water / 20% 250 mM of NaOH / 40% of 1 M CH₃COONa - 20 mM of
177 NaOH (37–45 min) The separation was performed within 45 minutes. Calibration was
178 performed with seven calibration points. This method allowed the simultaneous
179 identification of the following sugars: galactose (Gal), glucose (Glc), mannose (Man),
180 rhamnose (Rha), xylose (Xyl), arabinose (Ara), and glucuronic acid GlcA and galacturonic acid
181 (GalA).

182 **2.5. Determination of acetic acid by high performance liquid chromatography (HPLC)**

183 The acetic acid content of hemicelluloses was determined by adapting the protocol of Yuan
184 et al (2006). 1000 μ L of the oligosaccharide solution (10 mg in 5 mL of water)) were
185 saponified with NaOH (1250 μ L at 0.4 M) for 2 hours in the dark, at room temperature, in a 5
186 mL volumetric flask. The reaction was stopped by addition of H₃PO₄ at 0.4 M. This solution
187 was analyzed by high performance liquid chromatography coupled with a UV detector
188 (Shimadzu Prominence) using a Rezex™ RHM-Monosaccharide H⁺ (8%) column with sulfuric
189 acid (H₂SO₄ - 5.10⁻³ M) as the mobile phase with an isocratic flow rate of 0.8 mL.min⁻¹ and a
190 temperature of 60°C; the wavelength for detecting acetic acid was 210 nm. An external
191 calibration with 6 calibration points was performed.

192 **2.6. Steric Exclusion Chromatography**

193 Prior to the analysis, 5 mg of hemicelluloses were dissolved in 2.25 mL of 0.25 M NaNO₃.
194 Molecular weight distributions of hemicelluloses extracts were determined by size exclusion
195 chromatography coupled with a refractive index detector (Shimadzu Prominence). Two
196 columns coupled in series were used (Phenomenex GFC-P2000, 3000) to separate
197 hemicelluloses. The elution temperature was 35°C and the eluent consisted of 0.25 M
198 NaNO₃ with a flow rate of 0.7 mL.min⁻¹. Pullulan standards of known molar masses were
199 used for calibration.

200 **2.7. Fourier transform infrared spectroscopy**

201 The hemicelluloses obtained were subjected to Fourier Transform Infrared Spectroscopy
202 (FTIR) analysis. The infrared spectra were performed using a Thermo Scientific Nicolet 7600
203 IR-FT spectrometer over a frequency range between 4000 cm⁻¹ and 650 cm⁻¹.

204 **2.8. HSQC 2D NMR and calculation of the Degree of Acetylation (DS_{Ac})**

205 The 2-dimensional nuclear magnetic resonance (NMR) analyses of heteronuclear singular
206 quantum coherence (HSQC) were performed on a 400 MHz Bruker instrument with a
207 standard Bruker program. The hemicelluloses from the steam explosion and those extracted
208 by NaOH from the bleached wood were dissolved in 99.7% deuterium oxide (D₂O), while the
209 hemicelluloses extracted by DMSO from the bleached wood were dissolved in 99.9%
210 dimethyl sulfoxide d₆ (DMSO-d₆). The number of collected complex points was 1024 for the
211 1H-dimension with a relaxation of 1.5- and 256-time increments were recorded in 13C-
212 dimension. HSQC spectra were taken at room temperature.

213 The calculation of DS_{Ac} Xyl_p and DS_{Ac} Man_p are given below in Eq. 2 and 3.

214

215

216

$$\text{Eq 2. } DS(\text{Ac}) Xyl_p = \frac{[\text{Ac}]^a}{[\text{Man} + \text{Xyl}]^b} \cdot \frac{1}{1 + \frac{[\text{Man Ac}]^c}{[\text{Xyl AC}]^c}}$$

215

216

$$\text{Eq 3. } an_p = \frac{[\text{Ac}]^a}{[\text{Man} + \text{Xyl}]^b} - DS_{Ac} Xyl_p$$

217

218 Where a) Acetyl content determined by HPLC; b) Sugars content determined by HPEAC-PAD; c) Integration
219 ratio by HSQC-NMR

220

221 **3. Results and discussion**

222 **3.1. Composition**

223 The compositions of okoume sapwood (SW) and heartwood (HW) used in this study and
224 given in the Table 2 are in accordance with previous studies reported by Safou -Tchiama et
225 al. (2007). In the present study, a comparable amount of Klason lignin and glucose and a
226 substantially lower proportion of xylose and mannose was found.

227 **Table 2**

228 The polymeric hemicelluloses were recovered after SE of okoume SW and HW from the
229 liquid stream of the process by ethanolic precipitation and dialysis. Two different
230 impregnation conditions of wood sawdust prior to SE were examined (neutral and alkali
231 impregnation) and three different experimental conditions (170°C-10 min, 190°C-8 min,
232 210°C-5 min) in order to examine the influence of the treatment severity on the extract
233 yields and compositions. In this study the severity parameters (S) which combine
234 temperature and duration of the SE treatment have been used (see Material and Methods
235 section and Table 1). The condition sets used in this study were selected considering
236 previously described works (Chadni et al. 2019). For comparison purposes, hemicelluloses
237 were also recovered from okoume SW and HW holocellulose (after bleaching) with two
238 commonly used methods with DMSO and with sodium hydroxide. It was reported that alkali
239 solutions allow the extraction of hemicelluloses from bleached pulps with high yields
240 especially for xylans. Alkaline treatment can cleave ester groups of lignocellulosic complexes
241 in the cell wall and causes the swelling of cellulose facilitating the dissolution of
242 hemicelluloses. On the other hand, DMSO extraction is used for the recovery of slightly
243 modified hemicelluloses, close to their native structures but with lower yields (Evtuguin et
244 al. 2003). Naturally acetylated hemicelluloses have been isolated using this procedure.

245 **3.2. Hemicelluloses yields**

246 Fig. 2 gives the hemicelluloses yields recovered from SW and HW after precipitation and
247 dialysis for all the experimental conditions used in this study. As expected, from bleached
248 pulps, higher yields were observed for alkali extractions compared to DMSO method. It is
249 well known that unlike DMSO, alkali treatment can cleave ether and ester linkages between
250 polysaccharides and lignin and effectively releases hemicellulose. The hemicellulose yields
251 recovered by SE from non-bleached SW and HW are closed to those previously reported for
252 spruce and are between 2% and 6% w/w (Chadni et al. 2019). For the reasons mentioned

253 above, a basic impregnation of wood prior to SE has led to higher yields. However, in these
254 latter conditions and in accordance with previous works, an increase of the SE severity led to
255 a decrease of hemicelluloses yields due to degradation reactions such as peeling and alkaline
256 hydrolysis (Chadni et al. 2019, 2020).

257 **Fig.2**

258

259 **3.3. Sugar compositions and molecular masses**

260 The composition of the hemicelluloses isolated has been established in terms of monomeric
261 sugars by ionic chromatography after a controlled acidic hydrolysis (see experimental
262 section). The quantification of 4-*O*-MeGlcU being not possible by our chromatographic
263 method, its content was estimated by HSQC NMR (see section 3.5).

264 The average compositions in sugars corresponding to the 8 extraction conditions applied to
265 SW and HW are given in Table 1. The weight average molecular masses M_w of the
266 polysaccharides, assessed by water-based sized exclusion chromatography, are given in
267 Table 1. Number average (M_n) molecular weights and polydispersities are given in
268 Supplementary Data section S1. Whatever the experimental parameters and starting
269 materiel (SW or HW), for all the extractions involving alkaline conditions (classical alkali
270 extraction or SE after basic impregnation), hemicellulosic extracts were of high molecular
271 weights ($M_w \approx 60 - 100$ kDa) and mainly composed of xylose with a relatively high
272 proportion of 4-*O*-MeGlcU suggesting the recovery of polymeric glucuronoxylans (ratio 4-*O*-
273 MeGlcU / Xyl ≈ 0.35). Xylose was the predominant sugar accounting for 65% to 70% of total
274 amount of hemicellulosic sugars. It has been reported that in hardwood about 60% of non-
275 cellulosic sugars was xylose (Willfor et al. 2005).

276 Interestingly, it appears from Table 1 that glucuronoxylans of higher molecular masses were
277 recovered with NaOH-SE extraction compared to classical alkali extraction performed from
278 bleached pulp. This observation is in accordance with previous works, the structure of the
279 recovered hemicelluloses from SE being strongly influenced by the rapid pressure release
280 step which open the wood structure and limit the chemical degradations (Wojtasz-Mucha et
281 al. 2017).

282 The compositions of the extracts isolated with DMSO displayed a very different pattern. A
283 lower proportion of 4-*O*-MeGlcU was observed (ratio 4-*O*-MeGlcU / Xyl $\approx 0.05-0.08$).

284 Relatively high contents in mannose and glucose suggested the co-extraction of

285 glucomannans (GM). A difference in composition was clearly observed between SW and HW,
286 with a higher glucomannan content in SP. For H₂O-SE extraction, similar trends have been
287 observed with higher GM co-extraction. The relatively high GM content in SW was confirmed
288 from H₂O-SE extracts. GM have been reported to be the second most abundant
289 hemicellulose in hardwood (Sjöström, 1993). In addition, Willford et al. reported a relatively
290 high GM content in hardwood SW with varying proportions depending on the species.
291 Mannose accounted for about 10% of the sugars in *Populus deltoides* SW against only 1 to
292 2% in *Acacia crassicarpa* SP (Willford et al. 2005).

293 As expected the molecular masses of hemicelluloses extracted with DMSO and water-SE
294 were significantly lower. DMSO method solubilizes relatively low molecular mass
295 polysaccharide fragments. Teleman et al. 2003 extracted GM from birch and aspen wood
296 with DP \approx 16. Chadni et al. extracted galactoglucomannans from spruce by H₂O-SE in the
297 same range of severity, producing polysaccharides with comparable molecular masses (\approx 20
298 kDa) (Chadni et al. 2019, 2020). The relatively low molecular masses obtained using these
299 conditions are justified by the well-known acid-catalyzed hydrolysis of glycosidic linkages in
300 hemicellulose chains.

301 **Table 3**

302

303 **3.4. FTIR characterization**

304 FT-IR spectra of SE hemicelluloses from HW (H₂O-SE and NaOH-SE) are presented in Figure 3.
305 FT-IR spectra of the other hemicellulosic fractions isolated in this study are given in
306 Supplementary Data section S2. In H₂O-SE and DMSO extracts, the band at 1730 cm⁻¹ is due
307 to carbonyl groups stretching indicating that the hemicellulosic fractions isolated in neutral
308 conditions are acetylated. This observation was confirmed by the presence of high-intensity
309 band at 1244 cm⁻¹ assigned to C-O deformation bonds of ester functions (Rowley et al.,
310 2013). The bands at 1508 cm⁻¹ (δ_{C-C}) and 1460 cm⁻¹ (δ_{C-H} of CH₃-O groups of S and G units)
311 suggest the presence of a high amount of residual lignin in hemicelluloses extracted in basic
312 medium (Sun et al., 2012; Lv et al., 2013). It can also be observed that the band at 895 cm⁻¹,
313 assigned to C¹-H bonds of β -(1-4)-Xylp chain (Sun et al., 2016), is stronger in H₂O-SE. This is
314 in accordance with the higher xylose contents detected by HPAE-PAD in the H₂O-SE extracts
315 (section 3.3).

316 **Fig. 3**

3.5. NMR characterization and acetylation degree

317

318

319 The sugar compositions of the hemicellulosic fractions were confirmed by a 2D NMR study
320 ^1H - ^{13}C HSQC. The spectra were in good accordance with published data of GX and GM. For
321 HW, the main signals were assigned to sugar residues contained in GX (4-*O*-MeGlcUp and
322 Xylp) (Evtuguin et al. 2003, Teleman et al. 2003, Zhao et al. 2017). In SW spectra additional
323 cross-linked signals of lower intensities and assigned to Manp and Glcp were detected
324 attesting the presence of GM (Campestrini et al., 2013, Martínez-Abad et al. 2018). HSQC
325 NMR spectra of hemicellulosic fractions are given in Fig. 4 and in Supplementary Materials
326 section S3. The $^1\text{H}/^{13}\text{C}$ cross peaks assignments are given in Table 3.

327 **Fig. 4.**

328 **Table 3**

329 In accordance with the FT-IR data, NMR data showed that hemicelluloses recovered with
330 DMSO and H₂O-SE are all acetylated. This was confirmed by ^1H NMR intense signals at ^1H at
331 ≈ 2.0 - 2.2 ppm assigned to CH_3CO group (Supplementary Materials section S4). It has been
332 shown that the presence of acetylated sugar residues in the polysaccharides backbone
333 results in a large number of possible monosaccharide combinations and NMR cross-peaks
334 signals, complicating the spectra considerably (Michalak et al. 2018). In alkali conditions,
335 deacetylated polysaccharides were recovered because of a further deacetylation by
336 saponification reactions.

337 For DMSO and H₂O-SE hemicelluloses fractions, the acetylation degree was determined by
338 HPLC after saponification (Table 1). The $^{13}\text{C}/^1\text{H}$ HSQC NMR correlations also helped to
339 determine distribution patterns of *O*-acetyl groups in GM and GX backbone. Evtuguin et al.
340 (2003) determined the $^{13}\text{C}/^1\text{H}$ correlations of acylated heteroxylans backbone by
341 homonuclear (TOCSY) and heteronuclear (HSQC) NMR experiments. Campestrini et al.
342 (2013) characterized acetylated GM by NMR and other techniques. More recently, lignin
343 carbohydrate complexes (LCC) extracted from birch hardwood have been analyzed by 2D
344 NMR (HSQC and TOCSY). Martínez-Abad et al. (2018) described the assignment of the main
345 $^{13}\text{C}/^1\text{H}$ HSQC signals of partially acylated GX and GM in the LCC complex by HSQC NMR. In
346 this study, the ^1H and ^{13}C chemical shifts for the [*O*-Ac(1→2/3)- β -*D*-Xylp] and [*O*-Ac(1→2/3)-
347 β -*D*-Manp] are in good agreement with the values reported earlier. Based on previous
348 studies and using the data from NMR, HPLC and HPEA-PAD, a semi-quantification of *O*-2, *O*-3

349 and *O*-2,3 acetyl units in xylan and mannan backbones was performed (Giummarella et al.,
350 2017).

351 The results regarding the acetylation pattern are gathered in Table 4. In DMSO, very
352 different acetylation patterns were observed for SW and HW. Interestingly, SW
353 hemicelluloses are more highly acetylated than HW (4.1% and 1.0% respectively). A
354 comparable trend was observed for the water-SE extracts with significantly higher acetyl
355 contents (6.2% and 8.4% for HW and SW respectively). It has been previously reported that
356 hemicelluloses isolated from hardwood SW exhibited higher degree of branching and lower
357 xylose content (Xiao et al., 2020) but, to our knowledge, a comparison of the acetyl content
358 of SW and HW hemicelluloses has never been investigated. The higher acetylation degree of
359 SW hemicelluloses reported in the present study could be one of the factors contributing to
360 the higher porosity and water permeability of SW (Ramachandriya et al., 2014). In okoume
361 SP, comparable results were obtained for DMSO and H₂O-SE in terms of acetylation pattern.
362 Both GX and GM are *O*2 and *O*3 acetylated, the degree of acetylation being slightly higher
363 for GM compared to GX ($DS_{Ac} Manp \approx 0.25$ and $DS_{Ac} Xylp = 0.20$ respectively). For HW, a
364 significantly higher acetylation degree was also found for H₂O-SE compared to DMSO, GX
365 being acetylated at position *O*2 and/or *O*3 ($DS_{Ac} Xylp = 0.26$). These results are close to those
366 previously obtained from spruce and the recovery of galactoglucomannans (GGM) by H₂O-SE
367 with $DS_{Ac} \approx 0.27 - 0.35$, very similar to the values reported for native Ac-GGM Chadni et al.
368 2019, 2020. Thus, these results confirm that SE allowed to extract highly acetylated and
369 slightly modified polymeric hemicelluloses. The acetylation degree of hemicelluloses
370 strongly affecting the physico-chemical properties of the resulting materials (e.g. barrier
371 properties of films, Kishani et al., 2018), these experimental results could help to develop an
372 extraction route from okoume waste wood for the design of films and materials with
373 controlled properties.

374 **Table 4**

375

376 **4. Conclusion**

377 Steam explosion (SE) pretreatment was assessed for the extraction of high molecular weight
378 hemicelluloses directly from okoume SW and HW and compared to traditional extraction
379 methods with DMSO and alkali solution performed from bleached wood. The SE parameters
380 which include a short steaming duration and a mechanical defibration limit the

381 polysaccharide hydrolytic breakdown and enhance the efficiency of the subsequent
382 extraction. The recovery of high molecular weight GX was performed using a SE treatment
383 after basic impregnation. On the other hand, after a water pre-soaking, SE allowed the
384 recovery of a mixture of highly O2 and/or O3 acetylated GX and GM. It clearly appeared that
385 H₂O-SE preserved the acetyl moieties in a greater extent compared to the mild DMSO
386 extraction. The results obtained in our study showed that (1) SE can be employed for the
387 extraction of complex polysaccharides from wood for characterization purposes, (2) okoume
388 wood hemicelluloses are primarily composed of highly acetylated GX with a relatively high
389 amount of acetylated GM in the SW. The impact of this work could involve better recovery
390 of waste from the okoume industry in Gabon with a view to the production of hemicellulose-
391 based materials.

392

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Table 1. Composition of sugars, acetic acid (% of dry mass of hemicelluloses molar mass of hemicelluloses) and average (Mw in KDa) of hemicelluloses

Treatment	Impr ^a	S ^o ^b	Xyl ^c	GIUOMe ^d	Man ^c	Glc ^c	Ara ^c	Gal ^c	Rha ^c	GalA ^c	GlcA ^c	Ac ^e	Mw ^f	
NaOH ^e	SW		43.1 ± 1.0		n.a	1.7 ± 0.1	2.4 ± 0.1	1.7 ± 0.1	1.1 ± 0.0	2.9 ± 0.1	0.4 ± 0.0	-	64	
	HW		34.1 ± 2.6	11.1	n.a	0.1 ± 0.1	0.3 ± 0.0	1.4 ± 0.1	0.9 ± 0.0	1.6 ± 0.2	0.3 ± 0.0	-	56	
DMSO ^g	SW		16.0 ± 0.8	1.3	17.0 ± 0.6	27.4 ± 1.6	0.7 ± 0.0	1.5 ± 0.0	0.5 ± 0.0	1.1 ± 0.1	0.4 ± 0.0	4.1	29	
	HW		44.3 ± 0.3	2.2	11.5 ± 0.4	11.0 ± 0.2	0.2 ± 0.0	0.9 ± 0.0	0.7 ± 0.1	0.9 ± 0.0	0.3 ± 0.0	1.0	24	
Steam explosion ^h	SW	H ₂ O	3.1	47.7 ± 1.7	2.4	11.3 ± 0.8	9.3 ± 0.3	0.5 ± 0.0	5.4 ± 0.2	4.6 ± 0.1	5.4 ± 0.2	9.3 ± 0.2	8.4	9
		H ₂ O	3.6	44.5 ± 1.5		5.6 ± 0.2	25.7 ± 1.0	0.4 ± 0.0	4.4 ± 0.2	0.9 ± 0.1	0.9 ± 0.1	0.2 ± 0.0	8.1	26
		H ₂ O	3.9	29.4 ± 0.1		4.9 ± 0.0	34.3 ± 0.2	0.1 ± 0.0	3.4 ± 0.0	0.4 ± 0.0	0.5 ± 0.0	0.1 ± 0.0	8.0	21
	HW	H ₂ O	3.1	54.9 ± 11.7	1.1	2.6 ± 2.6	1.2 ± 0.8	2.2 ± 2.0	10.1 ± 5.5	1.9 ± 1.7	6.8 ± 0.2	0.8 ± 0.0	6.2	10
		H ₂ O	3.6	44.7 ± 2.1		2.3 ± 0.2	1.3 ± 0.1	0.1 ± 0.0	3.2 ± 0.2	0.1 ± 0.1	1.5 ± 0.2	0.2 ± 0.0	7.7	11
		H ₂ O	3.9	64.4 ± 1.9		4.2 ± 0.2	3.1 ± 0.1	0.1 ± 0.0	5.6 ± 0.2	1.5 ± 0.0	2.0 ± 0.1	0.3 ± 0.0	6.6	6
	SW	NaOH	3.1	30.7 ± 1.1	10.1	n.a	0.8 ± 0.0	1.4 ± 0.1	1.7 ± 0.1	1.4 ± 0.1	0.6 ± 0.0	0.4 ± 0.1	-	97
		NaOH	3.6	24.1 ± 1.3		0.2 ± 0.1	11.8 ± 0.7	1.7 ± 0.1	3.0 ± 0.2	1.7 ± 0.1	0.4 ± 0.0	0.2 ± 0.0	-	104
		NaOH	3.9	30.4 ± 0.1		0.2 ± 0.0	5.6 ± 0.0	1.6 ± 0.0	1.7 ± 0.0	0.3 ± 0.0	0.2 ± 0.0	0.2 ± 0.0	-	86
		NaOH	3.1	44.1 ± 1.0	15.9	n.a	0.3 ± 0.0	0.4 ± 0.0	1.0 ± 0.0	0.9 ± 0.0	0.8 ± 0.0	0.3 ± 0.0	-	64
HW	NaOH	3.6	29.0 ± 5.4		0.1 ± 0.1	0.2 ± 0.0	0.3 ± 0.1	1.4 ± 0.3	0.5 ± 0.1	0.5 ± 0.1	0.1 ± 0.0	-	69	
	NaOH	3.9	40.1 ± 6.3		0.1 ± 0.0	0.2 ± 0.0	0.4 ± 0.1	1.2 ± 0.2	0.4 ± 0.1	0.3 ± 0.0	0.1 ± 0.0	-	70	

^aImpregnation conditions prior to SE; ^b Severity factor of SE; ^cXylose, mannose, glucose, arabinose, galactose, Rhamnose, galacturonic and glucuronic acid %, determined after hydrolysis by HPEAC-PAD; ^destimation by HSQC-NMR; ^e acetic acid quantified by HPLC after saponification; ^f determined by SEC; ^gextraction from holocellulose; ^h extraction from wood by SE

Table 2. Chemical composition (% of dry wood) of raw wood.

	SW ^a	HW ^b
Extracts ^a	2.36 ± 0.31	2.00 ± 0.41
Klason lignin	29.68 ± 1.58	28.02 ± 0.37
Fuc	0.02 ± 0.00	0.00 ± 0.00
Rha	0,27 ± 0.04	0.24 ± 0.05
Ara	0.52 ± 0.04	0.11 ± 0.01
Gal	0.68 ± 0.01	0.56 ± 0.02
Glc	50.73 ± 0.15	54.19 ± 1.66
Xyl	11.34 ± 0.04	10.16 ± 2.41
Man	2.23 ± 0.03	2.09 ± 0.15
GalA	0.49 ± 0.28	0.64 ± 0.04
GlcA	0.13 ± 0.04	0.08 ± 0.07

Means of three independent analyses. ^aSapwood; ^bHeartwood; ^cToluene-ethanol-methanol extracts (see Material & methods section)

Table 3. Chemical shifts (ppm) of ¹H NMR spectra

	Impregnation	Structural Units	Attributions								
			1	2	3	4	5eq	5ax	6		
SW	NaOH	Xyl (isol.)	4.31	3.28	3.55				3.40		
		Xyl (Xyl-Ac)	4.42	3.23					3.35		
		αAra-3Xyl				4.27					
		MeGlcA		3.51	3.73	3.16	4.31				
	H ₂ O	Xyl (isol.)	4.31	3.8	3.57	3.79			3.40		
		Xyl (Xyl-Ac)	4.41	3.23	3.55	3.76			3.39		
		Xyl-3Ac	4.58	3.47	4.98	4.93					
		Xyl-2Ac		4.57	3.62	3.86					
		Xyl-2.3Ac			5.12	4.07					
		Xyl-2Ac-2MeGlcA			5.02						
		αAra-3Xyl	5.36			4.26					
		Xyl-2.3Ara	5.22								
		Man (Man-Ac)		4.03	3.65						
		Man-2Ac	4.88	5.44							
		Man-3Ac		4.17							
		MeGlcA	5.29	3.57	3.72				4.31		
		HW	NaOH	Xyl (isol.)	4.41	3.28					3.37
				Xy(Xyl-Ac)	4.42	3.23	3.53				3.36
				αAra-3Xyl				4.26			
Xyl-2.3Ara	5.23										
H ₂ O	MeGlcA			3.57	3.73	3.16			4.31		
	Xyl (isol.)		4.41	3.28	3.55	3.79			3.40		
	Xyl(Xyl-Ac)		4.42	3.23	3.54	3.76			3		
	Xyl-3Ac		4.56	3.49	5.0	4.93					
	Xyl-2Ac			4.57	3.62	3.88					
	Xyl-2.3Ac				5.12	4.04					
	Xyl-2Ac-2MeGlcA				5.01						
	αAra-3Xyl					4.27					
	Xyl-2.3Ara		5.23								
	Man (Man-Ac)			4.03	3.65						
	Man-2Ac		4.90								
Man-3Ac		4.17									
MeGlcA		3.57	3.72	3.16	4.31						

Xyl (isol.): non-acetylated Xylp unit in the skeleton isolated from another acetylated unit; Xyl (Xyl-Ac): non-acetylated Xylp unit linked with an acetylated neighbor; Xyl-3Ac: 3-O-acetylated Xylp unit; Xyl-2Ac: 2-O-acetylated Xylp unit; Xyl-2,3Ac: 2,3-di-O-acetylated Xylp unit; Xyl-3Ac-2GlcA: Xylp unit carrying a 2-O- and 3-O-acetylated MeGlcA; αAra-3Xyl: Ara terminal O-3 bonded to a monosubstituted Xylp unit; MeGlcA: O-2 bonded MeGlcA terminal residue; a-Ara-3Xyl: Ara terminal O-3 bonded to a monosubstituted Xylp unit; MeGlcA: O-2 bonded MeGlcA terminal residue to monosubstituted Xylp and also 3-O-acetylated.

Table 4. Acetylation degree of hemicelluloses

		Ac% ^a	DS _{Ac Manp} ^b	NMR $\delta C/\delta H$ ppm	DS _{Ac Xylp} ^c	NMR $\delta C/\delta H$ ppm
DMSO	SW	4.1	0,24	O-2 71.85/5.30 O-3-	0,18	O-2 73.85/4.52 O-3 75.45/4.82
	HW	1.0	0,02	O-2 - O-3 73.36/4.96	0,04	O-2 70.25/4.50 O-3 75.45/4.82
H ₂ O-SE	SW	8.4	0,25	O-2 73.66/5.28 O-3 75.47/5.19	0,20	O-2 71.02/4.50 O-2,3 72.00/4.84 O-3 77.13/4.64
	HW	6.2	0,08	O-2 73.13/5.25 O-3-	0,26	O-2 72.55/4.50 O-2,3 72.00/4.84 O-3 77.13/4.64

^aAc: Acetic acid (% of dry mass of hemicelluloses after saponification); ^bDS_{Ac Manp}: Degree of substitution of mannose residue with acetyl groups; ^cDS_{AcXylp}: Degree of substitution of xylose residue with acetyl groups.

Figure 1. Experimental procedures for hemicelluloses extraction from okoume sawdust

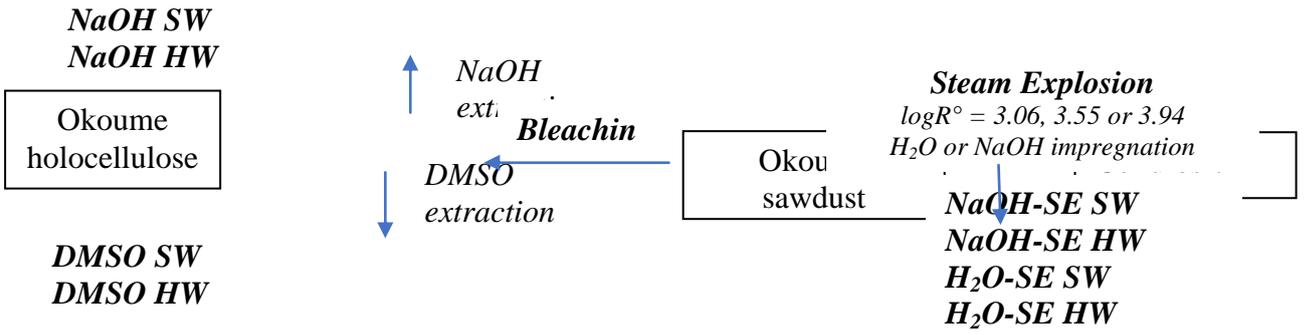


Figure 2. Polymeric hemicelluloses yields (% of dry mass of the initial wood)

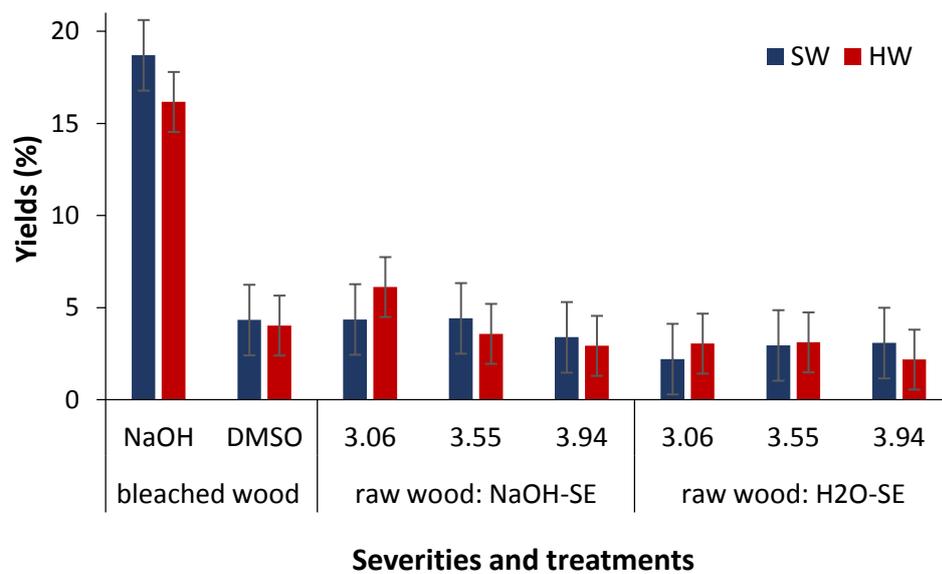


Figure 3. FT-IR Spectra of SE-extracted hemicelluloses (H₂O-SE HW and NaOH-SE HW, S = 3.1)

