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1 **D-xylose and L-arabinose laurate esters : enzymatic synthesis, characterization and**
2 **physico-chemical properties**

3
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14
15 **Abstract**

16 Efficient enzymatic synthesis of D-xylose and L-arabinose lauryl mono- and diesters has
17 been achieved by transesterification reactions catalyzed by immobilized *Candida*
18 *antarctica* lipase B as biocatalyst, in organic medium in the presence of D-xylose or L-
19 arabinose and vinyl laurate at 50 °C. In case of L-arabinose, one monoester and one
20 diester were obtained in a 57 % overall yield. A more complex mixture was produced
21 for D-xylose as two monoesters and two diesters were synthesized in a 74.9 % global
22 yield. The structures of all these pentose laurate esters was solved. Results
23 demonstrated that the esterification first occurred regioselectively onto the primary
24 hydroxyl groups. Pentose laurate esters exhibited interesting features such as low
25 critical aggregation concentrations values all inferior to 25 μM. Our study

26 demonstrates that the enzymatic production of L-arabinose and D-xylose-based esters
27 represents an interesting approach for the production of green surfactants from
28 lignocellulosic biomass-derived pentoses.

29

30 **Keywords:** D-xylose-laurate esters, L-arabinose laurate esters, lipase, surfactants,
31 biorefinery.

32

33 **1. Introduction**

34

35 For several years, there has been an increasing interest for bio-based
36 surfactants derived from annually renewable resources [1]. Among bio-based
37 surfactants, alkyl glycosides and sugar fatty esters are non-ionic surface active
38 compounds which present numerous advantages such as no toxicity for humans and
39 for the environment, biodegradability, absence of odor and color [2-4]. The main fields
40 of application of these non-ionic surfactants are related to personal care, cosmetics
41 and pharmaceutical applications as well as food emulsification in case of sugar fatty
42 esters [4-6]. The main alkyl glycosides and sugar fatty esters industrially produced or
43 described in literature were generally obtained from hexoses, especially D-glucose, or
44 hexose-based oligosaccharides such as sucrose, maltose and maltodextrins [1, 7].

45 D-xylose and L-arabinose are both pentoses abundantly present in
46 lignocellulosic plant cell walls and are main components of xylans [8]. The production
47 of new added-value molecules from pentoses represents a challenge for the
48 valorisation of lignocelluloses in the context of development of biorefineries [1, 7].

49 Xylose is currently reduced into xylitol, converted into furfural or fermented into
50 ethanol [7]. Although few pentose-based surfactants were previously developed, some
51 recent studies described the chemical synthesis of alkyl pentosides and pentose-based
52 fatty esters [9-13]. These syntheses often require high energy and various catalysts
53 that might not be compatible with green chemistry processes.

54 Classical chemical routes to the formation of fatty acid esters generally require
55 esterification or transesterification reactions and the use of polar solvents (DMF,
56 DMSO), a basic catalyst and high reaction temperatures (80-120°C) leading to complex
57 mixtures of monoesters, di- and higher esters as different regioisomers and unreacted
58 sugar [14]. The use of fatty esters or acyl chlorides in the presence of an organic
59 solvent and pyridine can improve the reaction yields but again with various degree of
60 substitution [15]. Selective protection of the hydroxyl groups of the carbohydrate
61 (acetyl, benzyl, isopropylidene) can orient the position of esterification reaction and
62 also sometimes to control the pyranose/furanose structure of the products [16].

63

64 The use of enzymes represents an interesting alternative for the preparation of
65 surfactants from biomass [7, 17]. For example, we previously described the enzymatic
66 synthesis and the surfactant properties of alkyl xylosides and alkyl oligoxylosides from
67 xylans and pretreated wheat bran using a transglycosylation approach with a
68 xylosidase (EC 3.2.1.37) or xylanases (EC 3.2.1.8) [18, 19]. Among well-known
69 biocatalysts, lipases (EC 3.1.1.3) were widely used to catalyze the ester bond formation
70 of sugar fatty esters[20, 21]. Enzymatic synthesis of sugar fatty esters is usually
71 achieved by esterification reaction from a carbohydrate and a fatty acid or by a

72 transesterification reaction from a carbohydrate and a fatty acid ester. Enzymatic
73 synthesis of sugar fatty esters with lipases represents a green alternative compared to
74 the conventional chemical approach [20]. Moreover, lipases can be used in
75 immobilized form, then allowing a recyclability and reusability of the biocatalyst thus
76 reinforcing the green alternative. Lipases display high regioselectivity compared to
77 chemical acylation decreasing the complexity of mixtures of regioisomers produced
78 [22-24]. During esterification, the amount of water present in reaction mixtures and
79 formed during reaction must be highly controlled as water induces hydrolysis of esters
80 products [25]. Hence, most of the lipase-based syntheses were performed in organic
81 media as water quantity can be controlled by the use of salts or molecular sieves as
82 desiccating agents [26, 27]. Transesterification catalyzed by lipases in presence of fatty
83 acid esters, especially vinyl esters, represents an interesting strategy to overcome the
84 water production during reaction and to induce better reactions yields. The main
85 disadvantage in this latter case is the production of acetaldehyde as a by-product but
86 the most widely employed lipases seem to be quite stable in the presence of
87 acetaldehyde [28].

88 Although enzymatic synthesis of hexose-derived fatty esters was extensively
89 described in the last twenty years, studies dealing with pentose-based fatty esters
90 were less reported in literature [22, 29-34]. Moreover, in most of the cases, structural
91 data related to these molecules are not described.

92

93 In the present paper, we report the successful enzymatic synthesis of laurate
94 pentose esters from D-xylose and L-arabinose catalyzed by the lipase B from *Candida*

95 *antarctica* (Novozym 435). Our strategy was based on transesterification reactions
96 with vinyl laurate and allowed producing different mono- and diesters from D-xylose
97 and L-arabinose. The structural features of these sugar esters were analysed by NMR
98 and mass spectrometry and their surface-active properties were evaluated.

99

100 **2. Experimental section**

101

102 *2.1. Materials*

103 2-Methylbutan-2-ol (2M2B, 99%), molecular sieves (4 Å, beads, 8-12 mesh), hexane
104 (>95%), tetrahydrofuran (THF), Novozym 435 (immobilized lipase acrylic resin from
105 *Candida antarctica*, Lot #SLBP0766V), vinyl laurate (>99%), orcinol, chloroform (99%)
106 and D-xylose (>99%) were purchased from Sigma-Aldrich Corp. (St. Louis, USA). L-
107 arabinose, acetic acid (AcOH, >99%), ethylacetate (EA, >99.8%), methanol (>99.9%),
108 petroleum ether (PE, >99.9%) and *n*-butanol (BuOH, >99%) were purchased from Roth
109 (Karlsruhe, Germany). Sulfuric acid (H₂SO₄, 95%) was purchased from VWR (Radnor,
110 USA). Acetonitrile (>99.9%) and propan-2-ol (>99%) were purchased from Carlo Erba
111 Reagents (Dasit Group S.p.A, Cornaredo, Italy).

112

113 *2.2. Methods*

114 *2.2.1. Enzymatic synthesis of D-xylose and L-arabinose laurate esters*

115

116 Enzymatic syntheses were carried out in screwed glass bottles with magnetic
117 stirrer, 400 x rpm, in an oil bath at 50 °C. Reactants, D-xylose or L-arabinose (50 mM)

118 and vinylaurate (150 mM) were incubated overnight with 2M2B and molecular sieves
119 (10% w/v). Reaction started when Novozym 435 was added to the medium at 1% w/v.
120 Reactions were stopped by incubating samples at 100 °C for 10 min and reaction
121 mixtures were centrifuged at 500 x g for 5 min in order to pellet molecular sieves and
122 enzymes. Supernatant was used to monitor, sugar fatty esters production by thin layer
123 chromatography and HPLC. Molecular sieves and enzymes were washed twice with
124 ultrapure water in order to collect residual pentoses (HPLC quantification).

125 Kinetic studies were achieved at 50 °C with 20 mL reaction mix and sampling
126 occurred at 1, 2, 4, 8, 24 and 48 hours of incubation, 1 mL of reaction mixture was
127 taken each time. These reactions were performed in triplicates.

128 Higher volume syntheses (100 mL) occurred in similar conditions in order to
129 produce sufficient quantities of products for purification and characterization.
130 Reactions were stopped after 4 hours of incubation at 50 °C.

131

132 Recycling of the lipase was assessed in presence of D-xylose or L-arabinose (50
133 mM), vinylaurate (150 mM), molecular sieves (10 % w/v) and Novozym 435 (1 % w/v).
134 Reaction was conducted during 4 h at 50°C under magnetic stirring (400 x rpm). After
135 4h, reaction was centrifugated (45 x g) and pellets containing the lipase and the
136 molecular sieves were further incubated with fresh D-xylose or L-arabinose and
137 vinylaurate. A total of 6 cycles of 4 h were performed.

138

139 *2.2.2. Purification, characterization and quantification of the transesterification*
140 *products*

141

142 The production of pentose fatty esters was investigated by TLC, using pre-
143 coated TLC-sheets ALUGRAM® Xtra SIL G/UV₂₅₄ (Macherey-Nagel GmbH & Co., Düren,
144 Germany) and BuOH : AcOH : water (2/1/1) as the mobile phase. Products were
145 revealed using 0.2 % (w/v) orcinol in H₂SO₄ (20 % v/v in water) and heating at 250 °C.

146 After removal of enzymes and molecular sieves, 2M2B was evaporated using a
147 rotary evaporator (Büchi Labortechnik AG, Flawil, Switzerland) and crude products
148 with remaining reactants were collected. Two hexane washings were then performed
149 to eliminate the remaining vinylaurate and a white paste was collected for both D-
150 xylose and L-arabinose-based esters. Vinylaurate removal was qualitatively assessed
151 by HPLC. Finally, the residual pentose was precipitated in THF (100 mL) leading to
152 soluble fractions containing mono- and diesters collected for further purification.
153 Residual pentose was finally solubilized in water (50 mL) and quantified by HPLC.
154 The purification of D-xylose or L-arabinose laurate esters was performed by silica gel
155 chromatography (9385 Merck Kieselgel 60, 230–400 mesh, 40–63 µm). Diesters were
156 eluted using PE / EA (7/3, v/v) and monoesters were eluted using pure EA. All the
157 products were obtained as a white crystalline powder.

158 NMR spectra were recorded on Bruker spectrometers (500 or 600 MHz for ¹H, 125 or
159 150 MHz for ¹³C). Chemical shifts are expressed in parts per million (ppm) using
160 tetramethylsilane as an internal standard. NMR spectra are presented as
161 supplementary data. Mass spectra (ESI-MS) and high resolution mass spectra (ESI-
162 HRMS) were performed on Q-TOF Micro micromass positive ESI (CV = 30 V).

163

164 **5-O-lauryl-L-arabinofuranose 1.** White solid, mp 130 °C. ¹H NMR (500 MHz, CDCl₃):
165 α/β = undetermined ratio, δ 5.30-5.35 (m, H-1α, H-1β), 4.20-4.35 (m, 2 H-5α, 2 H-
166 5β, H-4α or β), 4.05-4.15 (m, H-2α, H-2β, H-4α or β), 2.37 (t, *J* = 7 Hz, 2H), 1.60-1.66
167 (m, 2H), 1.25-1.35 (m, 16H), 0.90 (t, *J* = 7 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 174.8
168 and 174.4 (C=O α and β), 102.5 (C-1α), 95.9 (C-1β), 82.5 and 81.2 (C-4 α and β), 79.5
169 (C-3β), 77.6 (C-2α), 77.4 (C-3α), 76.1 (C-2β), 65.9 and 64.3 (C-5 α and β), 2D
170 experiment (HMBC): correlations between C=O and H-5; ESI-MS: 355.2 (M + Na)⁺; ESI-
171 HRMS : *m/z* calcd for C₁₇H₃₂O₆Na 355.2097, found 355.2089.

172

173 **3,5-di-O-lauryl-L-arabinofuranose 2.** White solid, mp 69 °C, ¹H NMR (500 MHz, CDCl₃) :
174 α/β = 1/1.56, δ 5.35-5.40 (m, H-1α, H-1β), 4.94 (t, *J* = 5 Hz, H-3β), 4.70 (dd, *J* = 5 Hz, *J* =
175 2 Hz, H-3α), 4.29-4.44 (m, H-5α, H-5β, H-4α), 4.23 (dd, *J* = 12 Hz, *J* = 5 Hz, H-5α), 4.13-
176 4.19 (m, H-2α, H-2β), 4.07-4.11 (m, H-4β), 2.38 (m, 2H), 1.59-1.65 (m, 2H), 1.20-1.38
177 (m, 16H), 0.90 (t, *J* = 7 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃):
178 δ 174.6, 174.4, 173.9 and 173.5 (2 C=O α and β), 102.9 (C-1α), 96.9 (C-1β), 81.2 (C-2),
179 81.0 (C-3 α), 79.9 and 79.8 (C-4α and C-3β), 79.1 (C-4β), 76.3 (C-2α and β), 65.0 and
180 63.4 (C-5 α and β), 2D experiments (HMBC): correlations between C=O 174.6 and
181 174.4 and H-3, C=O 173.9 and 173.5 and H-5; ESI-MS: 537.5 (M + Na)⁺; ESI-HRMS : *m/z*
182 calcd for C₂₉H₅₄O₇Na 537.3767, found 537.3773.

183

184 **5-O-lauryl-D-xylofuranose 3a.** White solid, mp 95 °C (lit. 93-95 °C [35]), ¹H NMR (600
185 MHz, CD₃OD): α/β = 1/1, δ 5.35 (d, *J* = 4 Hz, H-1α), 5.10 (d, *J* = 1 Hz, H-1β), 4.40 (dd, *J* =
186 11 Hz, *J* = 4 Hz, H-5β), 4.29-4.35 (m, H-4α and β), 4.27 (d, *J* = 4 Hz, H-5α), 4.25 (d, *J* = 4

187 Hz, H-5 β), 4.13-4.18 (m, H-3 α , H-5 α), 4.05 (dd, $J = 4$ Hz, $J = 2$ Hz, H-3 β), 3.96-3.98 (m,
188 H-2 β), 3.94 (t, $J = 4$ Hz, H-2 α), 2.34 (q, $J = 7$ Hz, 2H), 1.59-1.65 (m, 2H), 1.25-1.35 (m,
189 16H), 0.90 (t, $J = 7$ Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD): δ 175.5 and 175.4 (C=O α and
190 β), 104.3 (C-1 β), 97.8 (C-1 α), 82.2 (C-2 β), 80.9 (C-4 β), 78.2 (C-2 α), 77.7 (C-4 α), 74.8
191 and 74.6 (C-3 α and β), 65.4 (C-5 α), 64.7 (C-5 β), 2D experiment (HMBC): correlations
192 between C=O and H-5; ESI-MS: 355.3 (M + Na) $^+$; ESI-HRMS : m/z calcd for $\text{C}_{17}\text{H}_{32}\text{O}_6\text{Na}$
193 355.2097, found 355.2092.

194

195 **4-O-lauryl-D-xylopyranose 3b.** White solid, mp 96 °C, ^1H NMR (500 MHz, CD_3OD): α/β
196 = 2/1, δ 5.23 (d, $J = 3$ Hz, H-1 α), 4.85 (dd, $J = 8$ Hz, $J = 3$ Hz, H-4 β), 4.79 (td, $J = 8$ Hz, $J =$
197 5.5 Hz, H-4 α), 4.72 (d, $J = 6$ Hz, H-1 β), 4.14 (dd, $J = 12$ Hz, $J = 5$ Hz, H-5 β), 3.94 (t, $J = 8.5$
198 Hz, H-3 α), 3.72-3.83 (m, H-3 β , 2xH-5 α), 3.60 (d, $J = 8.5$ Hz, H-2 α), 3.47 (t, $J = 7$ Hz, H-
199 2 β), 3.38 (dd, $J = 12$ Hz, $J = 8.5$ Hz, H-5 β), 2.34 (q, $J = 6$ Hz, 2H), 1.58-1.65 (m, 2H), 1.25-
200 1.35 (m, 16H), 0.87 (t, $J = 7$ Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD): δ 173.7 (C=O α and β),
201 96.8 (C-1 β), 92.4 (C-1 α), 73.7 (C-2 β), 72.9 (C-3 β), 72.6 (C-2 α), 71.7 (C-3 α), 71.2 (C-
202 4 α), 71.1 (C-2 β), 62.0 (C-5 β), 59.7 (C-5 α), 2D experiment (HMBC): correlations
203 between C=O and H-4; ESI-MS: 327.2 (M + H) $^+$, 355.2 (M + Na) $^+$, 385.1 (M + K) $^+$; ESI-
204 HRMS : m/z calcd for $\text{C}_{17}\text{H}_{32}\text{O}_6\text{Na}$ 355.2097, found 355.2089.

205

206 **2,5-di-O-lauryl-D-xylofuranose 4.** White solid, mp 79 °C, ^1H NMR (600 MHz, CDCl_3):
207 $\alpha/\beta = 1/4.5$, δ 5.65 (d, $J = 4$ Hz, H-1 α), 5.27 (broad s, H-1 β), 5.07 (d, $J = 1$ Hz, H-2 β), 4.93
208 (t, $J = 4$ Hz, H-2 α), 4.56 (td, $J = 9$ Hz, $J = 4.5$ Hz, H-5 β), 4.48 (dd, $J = 12$ Hz, $J = 5$ Hz, H-
209 5 α), 4.42 (q, $J = 5$ Hz, H-4 α), 4.39 (dd, $J = 5$ Hz, $J = 4$ Hz, H-3 α), 4.24-4.29 (m, H-5 β , H-

210 4 β), 4.17 (dd, $J = 12$ Hz, $J = 5$ Hz, H-5 α), 4.14-4.16 (m, H-3 β), 2.30-2.39 (m, 4H), 1.58-
211 1.62 (m, 4H), 1.19-1.39 (m, 32H), 0.90 (t, $J = 7$ Hz, 6H); ^{13}C NMR (150 MHz, CDCl_3): δ
212 175.0 (C=O β), 174.3 (C=O α), 173.8 (C=O α), 172.8 (C=O β), 100.9 (C-1 β), 95.3 (C-1 α),
213 81.1 (C-2 β), 80.7 (C-4 β), 79.9 (C-2 α), 76.7 (C-4 α), 74.2 (C-3 α), 73.6 (C-3 β), 62.6 (C-5 β),
214 62.3 (C-5 α), 2D experiment (HMBC): correlations between C=O (175.0 and 174.3) and
215 H-2, and between C=O (173.8 and 172.8) and H-5; ESI-MS: 537.5 (M + Na) $^+$; ESI-HRMS :
216 m/z calcd for $\text{C}_{29}\text{H}_{54}\text{O}_7\text{Na}$ 537.3767, found 537.3759.

217

218 **3,5-di-O-lauryl-D-xylofuranose 5**. White solid, mp 77 °C, ^1H NMR (500 MHz, CDCl_3):
219 $\alpha/\beta = 1/0.2$, δ 5.47 (d, $J = 4$ Hz, H-1 α), 5.28 (d, $J = 1$ Hz, H-1 β), 5.17 (dd, $J = 5$ Hz, $J = 3$
220 Hz, H-3 α), 5.11 (dd, $J = 5$ Hz, $J = 2$ Hz, H-3 β), 4.54-4.60 (m, H-4 α , H-4 β), 4.25-4.33 (m, 2
221 H-5 β), 4.10-4.22 (m, 2 H-5 α , H-2 α , H-2 β), 2.25-2.35 (m, 4H), 1.55-1.64 (m, 4H), 1.20-
222 1.28 (m, 32H), 0.80 (t, $J = 7$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3): δ 173.80 (C=O α), 173.7
223 (C=O β), 173.5 (C=O α and β), 103.1 (C-1 β), 96.0 (C-1 α), 80.6 (C-2 β), 78.6 (C-3 α), 78.3
224 (C-3 β), 77.8 (C-4 β), 75.7 (C-2 α), 75.0 (C-4 α), 63.1 (C-5 β), 62.2 (C-5 α), 2D experiment
225 (HMBC): correlations between C=O (173.8 and 173.5) and H-3, and between C=O
226 (173.7 and 173.5) and H-5; ESI-MS: 537.5 (M + Na) $^+$; ESI-HRMS : m/z calcd for
227 $\text{C}_{29}\text{H}_{54}\text{O}_7\text{Na}$ 537.3767, found 537.3777.

228

229 The quantification of sugar fatty esters was performed by HPLC using a NUCLEOSHELL[®]
230 RP 18 ec, 5 μm 250 x 4.6 mm (Macherey Nagel) column at 40 °C. Purified products
231 were used as standards. Mono- and diesters were eluted at 0.6 mL.min $^{-1}$, at 40 °C and
232 with an acetonitrile (**A**)/water (**B**) mobile phase, 0-5 minutes 80 % **A** and 20 % **B**, 5-20

233 minutes 80 to 100 % **A** and 20-30 minutes 100 % **A**. The detection was performed with
234 a dynamic light scattering detector (PL-ELSD 1000, Polymer Laboratories) at 40 °C
235 under 350 kPa azote pressure.

236 Retention times were determined for each ester **1**: 6.7 min, **2**: 31.5 min, **3a-b** (not
237 separated in these conditons) : 6.2 min, **5**: 28.9 min and **4**: 30.4 min.

238 The quantification of residual sugars was also performed by HPLC using a
239 NUCLEODUR® 100-5 NH₂-RP, 5 µm 250 x 4 mm (Macherey Nagel) column at 40 °C.
240 Pure sugars were used as standards. Sugars were eluted at 1 mL.min⁻¹, at 40 °C and
241 with an acetonitrile (A)/water (B) mobile phase 75/25 % in isocratic flow. The detection
242 was performed with a dynamic light scattering detector (PL-ELSD 1000, Polymer
243 Laboratories) at 40 °C under 350 kPa azote pressure. Retention time of D-xylose and L-
244 arabinose were 4.5 and 4.2 minutes respectively.

245

246 *2.2.3. Determination of D-xylose and L-arabinose laurate esters surface-active*
247 *properties*

248

249 Adsorption to an air-aqueous medium interface was analysed at 25.0 ± 0.2 °C
250 with an automated Langmuir Balance system equipped with a Wilhelmy plate (KSV
251 minitrough, KSV instruments Ltd., Helsinki, Finland). Purified sugar esters, or mixtures
252 of esters (extracted from crude reactions of 4 hours at 50 °C with no further
253 purification of mono- and diesters) were solubilized in DMSO and injected (20 µL) into
254 the subphase (Tris HCl 10 mM pH 7) to a range of final concentrations (C). Injections
255 were done using a Hamilton syringe and two homemade devices allowing the injection

256 of the product without disturbing the air-water interface. These devices were placed at
257 two fixed positions on the trough to ensure a reproducible injection process. The
258 subphase was stirred, during the whole experimentation, using two cylindrical
259 micromagnetic rods ($8 \pm 1.5 \text{ mm}^2$) and two electronic stirrer heads located beneath
260 the trough (model 300, Rank Brothers, Bottisham, U.K.). Stirring was performed at 100
261 x rpm with an auto-reverse movement. The increasing of the surface pressure was
262 recorded right after the injection until its value reaches equilibrium ($\Delta\Pi_{\text{eq}}$). CAC was
263 determined from the plot $\Delta\Pi_{\text{eq}} = f(C)$ at the intersection between the linear
264 regression of the ascendant and plateau parts

265

266 2.2.4. *pH stability investigation*

267

268 The pH stability of purified molecules was investigated by performing
269 incubation at room temperature of 5 mM aqueous solutions of purified products at pH
270 varying from 4 to 9. Citrate phosphate buffer 50 mM was used to prepare pH solutions
271 from 4 to 8 and borate buffer 50 mM was used to prepare pH 9 solution. Stability was
272 monitored, during 72 hours with regular sampling (1, 2, 4, 8, 24, 48 and 72 hours),
273 qualitatively by TLC and quantitatively by HPLC.

274

275 **3. Results**

276

277 Transesterification reactions between L-arabinose or D-xylose and vinylaurate
278 were performed with immobilized *C. antarctica* lipase B, commercially known as

279 Novozym 435. Various conditions were tested (substrates and lipase loading, organic
280 solvents) and led to the choice of reaction parameters (data not presented) to carry
281 out the enzymatic catalysis: L-arabinose or D-xylose (50 mM) and vinyl laurate (150
282 mM) with molecular sieves (10 % w/v) in screwed glass bottles for various incubation
283 times with 2M2B as solvent and magnetic stirring (400 x rpm).

284

285 3.1. *Enzymatic synthesis of L-arabinose laurate esters*

286

287 Products of transesterification reactions at 50 °C were first visualized by TLC,
288 indicating that a mixture of monoester **1** and diester **2** of L-arabinose was obtained.
289 Those esters were purified from 100 mL reactions performed during 4 hours with
290 conditions described above.

291 After purification by flash chromatography over silica gel and a careful NMR study, the
292 structure of monoester **1** was attributed to 5-*O*-lauryl-L-arabinofuranose and the
293 structure of diester **2** to 3,5-di-*O*-lauryl-L-arabinofuranose as mixtures of α/β anomers
294 (Figure 1A). Global conversion of L-arabinose was evaluated by HPLC by measuring L-
295 arabinose remaining after 4 hours in reaction media. From a 100 mL reaction at 50 °C,
296 320 and 756 mg of L-arabinose lauryl monoester **1** and diester **2** were respectively
297 recovered corresponding to a conversion of 49.0 % of introduced L-arabinose and a
298 yield of 48.6 % (19.2 % of monoester **1** and 29.4 % of diester **2**).

299 Kinetic of formation of L-arabinose lauryl esters obtained at 50°C was evaluated for 48
300 hours by HPLC with 20 mL reactions (Figure 1B). During acylation of L-arabinose, both
301 monoester **1** and diester **2** were formed during the first hour of the reaction (Figure 2)

302 and were produced at $2.8 \pm 0.1 \text{ mg.mL}^{-1}$ and $3.2 \pm 0.3 \text{ mg.mL}^{-1}$ respectively. Maximal
303 quantities of L-arabinose lauryl esters were detected after 4 hours of catalysis and
304 were equivalent to 4.0 ± 0.1 and $9.1 \pm 0.3 \text{ mg.mL}^{-1}$ for **1** and **2** respectively,
305 corresponding to a conversion of $59.2 \pm 1.5 \%$ of introduced L-arabinose and a 56.8 %
306 yield (22.8 % of monoester **1** and 34.0 % of diester **2**). After 4 hours of reaction, a slight
307 decrease in concentration of diester **2** was observed maybe due to a slight hydrolysis.

308

309 3.2. *Enzymatic synthesis of D-xylose laurate esters*

310

311 For the transesterification reactions of D-xylose with vinyl laurate at 50 °C
312 during 4h, two sets of spots were detected by TLC indicating the formation of a
313 complex mixture of both monoesters and diesters. From 100 mL reactions, one major
314 monoester **3a** was separated by flash chromatography and NMR data assigned its
315 structure to the 5-*O*-lauryl-D-xylofuranose, as a mixture of anomers. A minor
316 monoester **3b** was also detected and its structure was attributed to 4-*O*-lauryl-D-
317 xylopyranose. Two diesters **4** and **5** were purified by flash chromatography over silica
318 gel. The less polar diester **4** was identified as 2,5-di-*O*-lauryl-D-xylofuranose and the
319 more polar diester **5** as 3,5-di-*O*-lauryl-D-xylofuranose as mixtures of anomers (Figure
320 2A). From 100 mL reactions, a global conversion of 53 % of initial D-xylose was
321 reached. After separation by chromatography, 340 mg of monoesters (20.5 %) and 557
322 mg of diesters **4** and **5** (25.5 %) were purified and a global yield of 45.5 % was
323 obtained.

324 Kinetic studies were performed during 48 hours in 20 mL reactions. During acylation
325 reactions of D-xylose, the first products formed were monoesters **3a-b** 3.3 ± 0.3
326 mg.mL^{-1} during the first two hours of the reaction (Figure 2B). After the third hour, the
327 two diesters appeared with quantities of $4.8 \pm 0.1 \text{ mg.mL}^{-1}$ for **5** and $4.0 \pm 0.1 \text{ mg.mL}^{-1}$
328 for **4** whereas the production of **3** reached $6.2 \pm 0.1 \text{ mg.mL}^{-1}$. The maximal production
329 of xylose lauryl monoesters occurred in 4 hours while the maximal yield of diester was
330 attained after 24 hours. Global conversion of D-xylose was evaluated by HPLC by
331 measuring D-xylose remaining after 4 hours in reaction media and attained 77.1 ± 2.0
332 % and a 74.8 % global overall yield (4h) (38.4% of monoesters **3**, 19.4% of diester **4** and
333 17.4 % of diester **5**). Conversion of D-xylose was higher compared to this obtained with
334 the 100 mL reaction probably due to a better mass transfer.

335 Assays of recycling the enzyme were conducted in the same conditions, by
336 performing transesterification of D-xylose and vinyl laurate during 4 hours at 50 °C.
337 Every 4 hours, the reaction medium and the immobilized enzyme were separated.
338 Reaction medium was analysed by HPLC and the remaining enzyme was used to
339 perform another round of transesterification reactions with fresh D-xylose (50 mM)
340 and vinyl laurate (150 mM). HPLC analysis showed that the Novozym 435 was re-usable
341 for 5 cycles without losing significant efficiency. During the sixth cycle, the synthesis of
342 total D-xylose laurate esters reached 5 % of synthesis occurring during each previous
343 cycle indicating a drastic loss of lipase efficiency (data not presented). Similar results
344 were obtained for recycling experiments in presence of L-arabinose.

345

346 *3.3. pH stability of L-arabinose and D-xylose laurate esters*

347

348 The pH stability of the purified sugar esters produced at 50 °C was investigated
349 by incubating aqueous solutions with pH range from pH 4 to 9. L-arabinofuranose and
350 D-xylofuranose laurate esters solutions were incubated at room temperature and
351 samples were taken during 72 hours. The evaluation of the stability was studied by
352 HPLC (data not shown). The L-arabinofuranose and D-xylofuranose laurate esters were
353 stable in solution within a pH range from 4 to 9 as no liberation of pentose indicating a
354 hydrolysis of the ester bonds was detectable.

355

356 **3.4.** *Surface-active properties of xylose and arabinose laurate esters*

357

358 Surface-active properties were investigated for pentose esters produced at 50
359 °C. The ability of pentose esters to adsorb to an air-aqueous medium interface was
360 studied by measuring the surface pressure increase further to the injection of the
361 esters in the aqueous subphase. Figure 3 shows as an example the adsorption kinetics
362 of monoester **3a**. Similar results were obtained for the other esters. For concentration
363 below 2 μM, no surface pressure increase was observed, suggesting that at very low
364 concentration in the subphase, the adsorption of monoester **3a** to the air–water
365 interface was too low to exert an effect on the surface pressure. At concentration ≥ at
366 3 μM, a surface pressure increase can be observed indicating that the monoester was
367 able to adsorb at the air-aqueous medium interface. Before the detection of the
368 surface pressure increase, there was a lag time, depending on the concentration
369 (Figure 3). This suggests that the adsorption to the air–aqueous medium interface is

370 increased according to monoester **3a** concentration, indicating a higher probability of
371 interactions between the ester molecules at the interface [36]. The higher number of
372 molecules at the interface also explains the higher equilibrium surface pressure
373 reached at the plateau.

374 Critical aggregation concentrations (CAC) were determined for purified D-xylofuranose
375 and L-arabinofuranose monoesters and for mixtures of D-xylofuranose or L-
376 arabinofuranose mono- and diesters (Table 1). For pure compounds, the surface
377 pressure was measured for a range of concentrations going from 1 μM to 35 μM in the
378 aqueous subphase (pH 7, room temperature) (Figure 4). As pure D-xylofuranose
379 diesters **4** and **5** or L-arabinofuranose diester **2** showed an extreme hydrophobic
380 behavior (no solubility in aqueous media) for concentrations superior to 2 μM , no
381 measurement of CAC was possible for these molecules. D-xylofuranose monoester **3a**
382 and L-arabinofuranose monoester **1** presented respectively a CAC of $11.5 \pm 1.6 \mu\text{M}$ and
383 $8.4 \pm 0.9 \mu\text{M}$ (Figure 4A and 4B). In case of xylose or arabinose esters mixtures, CAC
384 were estimated to $23.4 \pm 2.3 \mu\text{M}$ and $11.8 \pm 0.7 \mu\text{M}$ respectively (Figure 4C and 4D).

385

386 **4. Discussion**

387

388 Numerous studies from literature deal with esterification and
389 transesterification reactions catalysed by lipases for hexoses acylation, mainly D-
390 glucose. In this context, the selective acylation of the primary hydroxyl group for
391 hexoses and the formation of 6-O acylhexopyranoses is well known [21, 22, 37].

392 The enzymatic transesterification of L-arabinose was previously described with
393 a lipase from *Pseudomonas cepiaca* using oxime esters as acyl donors [38]. The
394 reaction resulted in the selective formation of the 5-*O* monoacylated L-
395 arabinofuranose in 45-70 % yield according to the length of the acyl chain [38]. In a
396 recent study, the synthesis of 5-*O*-palmitoyl-L-arabinofuranose monoester was
397 obtained by esterification reaction with lipase N435 [34]. The regioselective acylation
398 onto the most reactive primary hydroxyl position of the furanose isomer of L-arabinose
399 was also obtained in the present study. However, in our reaction conditions, the
400 diester **2** was also produced as the major compound in addition to the monoester **1**.

401 In case of D-xylose, lipase-catalysed esterification is described to yield complex
402 mixtures of products with immobilized lipase of *C. antarctica* and lipase of *Candida*
403 *rugosa* [32]. In previous studies, lipase-catalysed synthesis of fatty acid xylose esters
404 was investigated but no information concerning neither the regioselectivity of the
405 reaction nor the structures of the esters were available [32, 33, 39]. Lipase-catalysed
406 esterification of 1,2-*O*-isopropylidene- α -D-xylofuranose with various fatty acids was
407 studied. After deprotection of the acetal, selective synthesis of 5-*O*-acyl D-xylofuranose
408 occurred [30, 31, 40]. Solvent-free esterification reactions at 75 °C with *Rhizomucor*
409 *miehei* lipase and 1,2-*O*-isopropylidene- α -D-xylofuranose as acyl acceptor were carried
410 out with fatty acids (lauric to arachidonic acid) and N435 as biocatalyst at 50 °C [40].
411 Conversion rate of the protected xylose reached 50 % after 24 hours with arachidonic
412 acid.

413 In the present study, esters produced from D-xylose and L-arabinose at 50 °C
414 were present as furanose isomers except a minor monoester **3b** for D-xylose as a

415 pyranose isomer. No diesters in pyranosic form were detected and no acylation on the
416 anomeric position occurred. This indicates that esterification first took place
417 regioselectively onto the primary hydroxyl group. The pyranose / furanose equilibrium
418 that should exist in the reaction mixture is displaced by the better reactivity of the
419 primary hydroxyl group. Further esterification on a secondary hydroxyl group occurred
420 with monoesters as substrates for the lipase. Indeed, experiments conducted with
421 monoester **3a** as acyl acceptor at 50 °C (in the conditions described in section 2.1.1)
422 showed that, after 2 hours of reactions, diesters **4** and **5** were obtained in the same
423 ratio (data not shown). For both pentoses, kinetic studies revealed that maximum
424 yields were obtained at 50 °C after 4 hours of reaction for xylose monoesters **3** and
425 arabinose monoester **1** and diester **2** and after 24 hours for xylose diesters **4, 5**, with a
426 higher conversion rate for D-xylose. However, D-xylose-based esters production was
427 slower during the first two hours of reaction compared to L-arabinose. This could be
428 explained by the lower ratio of the furanose isomers for D-xylose compared to L-
429 arabinose in the reaction mixture as it is the case in aqueous solution [41] or by a
430 difference in dissolution kinetics as described for D-glucose and D-fructose in 2M2B
431 [42]. Monoesters **1** and **3a** can undergo a second acylation reaction. For L-arabinose,
432 only diester **2** resulting from a transesterification reaction on the hydroxyl group at C-3
433 was synthesized and was already detected in the first hour of the reaction at 50°C. No
434 evolution of the monoester / diester ratio was observed during the reaction course
435 even after 48 hours. In comparison, the reaction was more complex for D-xylose, as
436 two diesters **4** and **5** were obtained from monoester **3**. The second acylation proved to
437 be less selective and slower than for L-arabinose. These results could be rationalized

438 by an enhanced reactivity of the secondary hydroxyl groups on C-3 compared to the C-
439 2 position for both monoesters **1** and **3a**. Indeed, for both monoesters, a second
440 acylation was observed at C-3 position. However, for D-xylose monoester, the
441 acylation on C-3 position could be in competition with acylation at C-2 maybe due to
442 the *cis*-relationship(s) between OH in C-3 position and the acylated C-5 position which
443 could generate steric hindrance.

444 The surface-active properties of the pentose-based esters produced a 50 °C can
445 be compared to other sugar-based laurate esters described in literature. The CAC
446 values were rather similar to those for xylofuranose laurate monoester for which CMC
447 value of 41 μM or 18 μM have been determined [43, 44]. Other laurate esters with
448 different polar heads have shown variable CMC or CAC values depending on the polar
449 head, such as maltopyranose and glucopyranose laurate ester with respective CMC
450 values of 120 μM and 180 μM [44]. A CMC value of 3 mM was obtained for
451 galactopyranose laurate esters [45]. Measurement of CMC/CAC is highly dependent on
452 the pH and the temperature conditions. The CAC values obtained for our pentose-
453 based laurate esters are inferior to 100 μM compared to hexose-based laurate esters
454 and these low values could be related to the lower hydrophobicity of the smaller polar
455 heads (pentoses vs. hexoses) [46].

456 The low CAC values of the D-xylofuranose and L-arabinofuranose esters produced in
457 the present study indicate that these molecules present interesting surfactant
458 properties as their CAC are lower than those of commercially available sugar esters
459 such as Tween 20 (80 μM). Furthermore, the mixtures of esters also exhibit low CAC

460 values which are of interest in a context of an industrial production with limited
461 purification steps.

462

463 **5. Conclusions**

464

465 This study dedicated to the lipase-catalysed synthesis of fatty esters from two
466 biomass-derived pentoses, D-xylose and L-arabinose, reports the full characterization
467 of the esters produced and a better understanding of the regioselectivity of the lipase-
468 catalysed transesterification with both pentoses. In this work, the enzymatic synthesis
469 of D-xylose and L-arabinose laurate esters using *C. antarctica* lipase B (N435) as a
470 biocatalyst was reported. Both L-arabinose and D-xylose gave rise to the synthesis of
471 pentose laurate esters as furanose isomers indicating a regioselective first acylation
472 onto the primary hydroxyl group. A second acylation could then occur either
473 selectively on *O*-3 for L-arabinose or as a mixture of diacylated products on *O*-2 and *O*-
474 3 positions for D-xylose. The nature of the pentose influenced kinetics of production
475 and obtained yields. Kinetics of synthesis of D-xylose based esters were slower but
476 yields were higher than those obtained for L-arabinose based esters.

477 Investigation of surfactant properties of pentoses laurate esters indicated that D-
478 xylose and L-arabinose mono- and diesters exhibited good surfactant properties, such
479 as low CAC, whether purified or in mixtures.

480 Our study allowed developing a green route for the one step functionalization
481 of pentoses from lignocellulosic biomass to produce sugar esters that could be useful
482 as surfactants for various applications (cosmetics, phytochemistry, food ...).

483

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485

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627

628 **Figures Captions**

629 Figure 1. (A) Transesterification reaction of L-arabinose and vinylaurate performed by
630 the lipase Novozym435. (B) Kinetics of synthesis of arabinose laurate esters quantified
631 by HPLC. Reactions were performed at 50°C during 48h with 50 mM arabinose, 150
632 mM vinylaurate, 1% (w/v) lipase. **1**: arabinose laurate monoester, **2**: arabinose laurate
633 diester.
634

635 Figure 2. (A) Transesterification reaction of D-xylose and vinylaurate performed by the
636 lipase Novozym435. (B) Kinetics of synthesis of xylose laurate esters quantified by
637 HPLC. Reactions were performed at 50°C during 48h with 50 mM xylose, 150 mM
638 vinylaurate, 1% (w/v) lipase. **3a-b**: xylose laurate monoesters, **4** and **5**: xylose laurate
639 diesters.
640

641 Figure 3. Surface activity of the xylose laurate monoester **3a**. Kinetics of monoester
642 adsorption at the air-water interface, time zero corresponds to the injection into the
643 subphase
644

645 Figure 4. CAC determination of purified arabinose and xylose laurate monoesters **1** and
646 **3** (A and B respectively) and of mixtures of mono- and diesters of arabinose or xylose
647 (C and D respectively). Results obtained at room temperature using a Langmuir
648 balance equipped with a Wilhelmy platinum plate.
649

650 Table 1. CAC values were measured for pure esters **1** and **3a** whereas in case of
651 mixtures CAC values were determined with an average molecular weight of each
652 compound.
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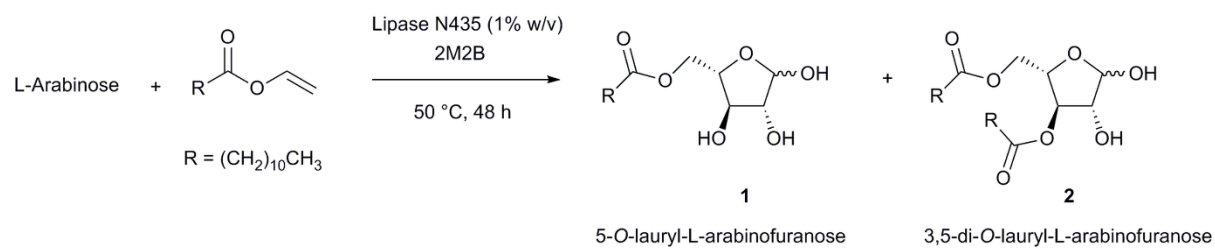
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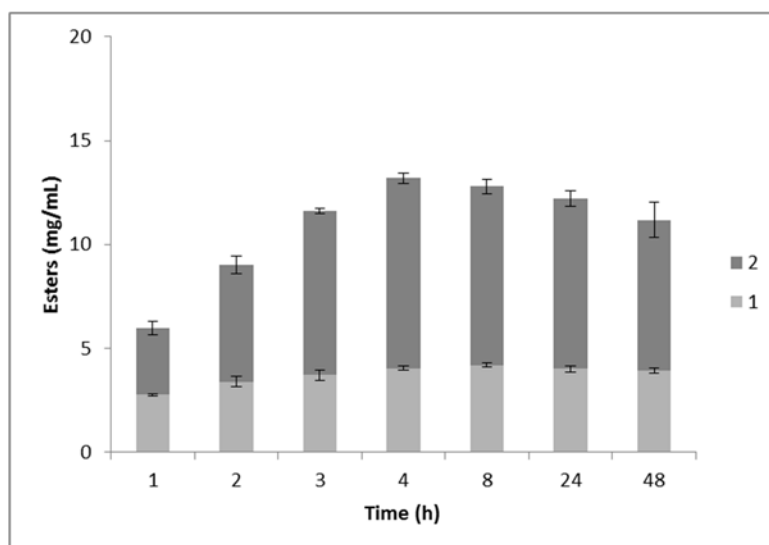
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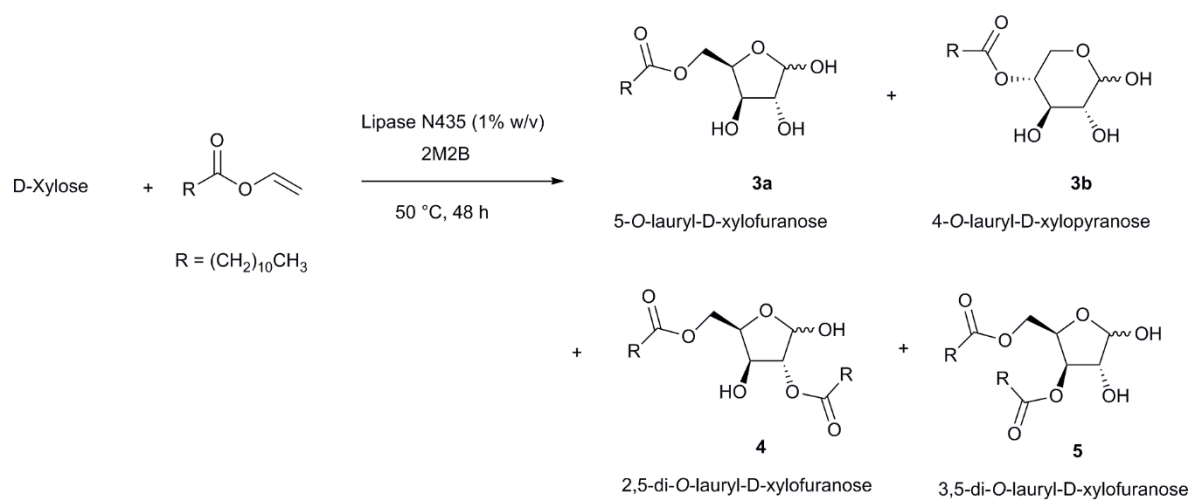
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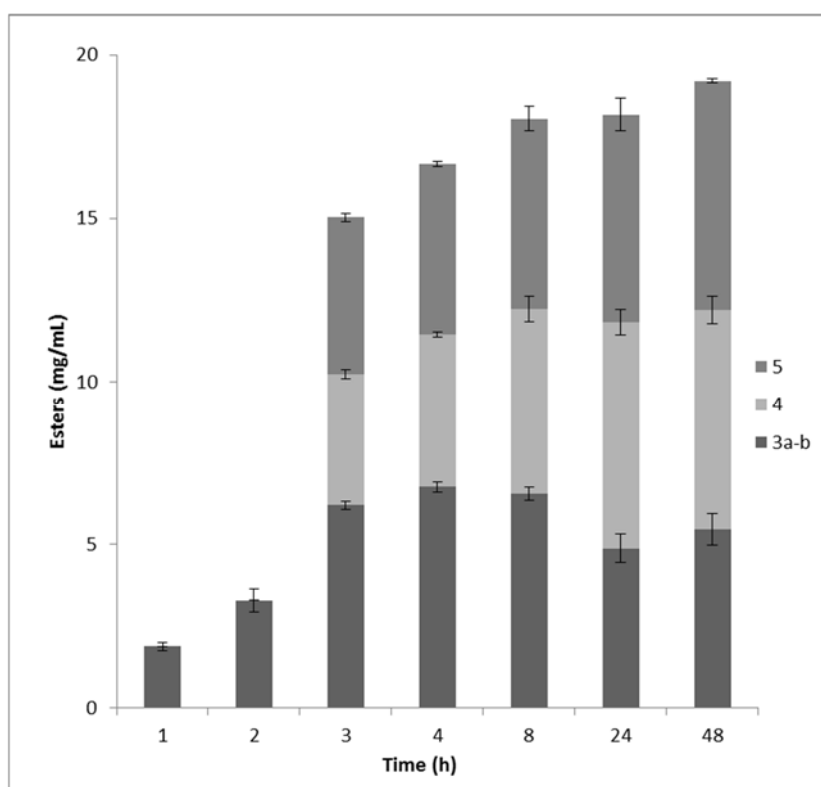
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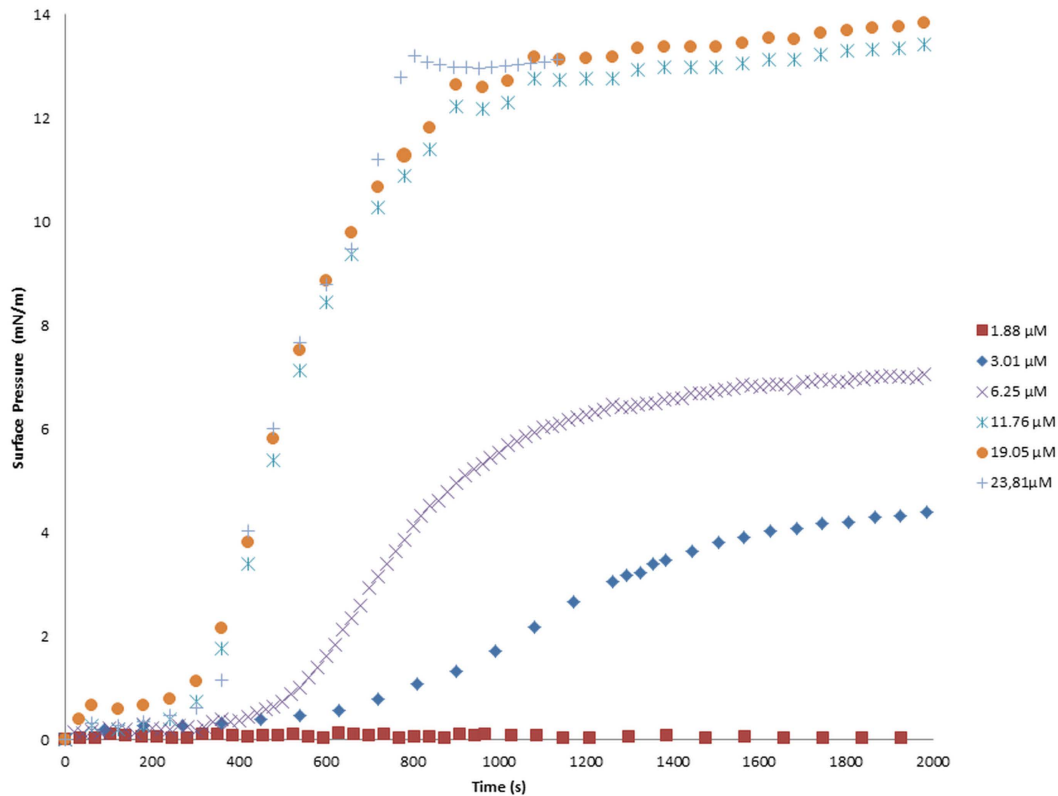


A



B





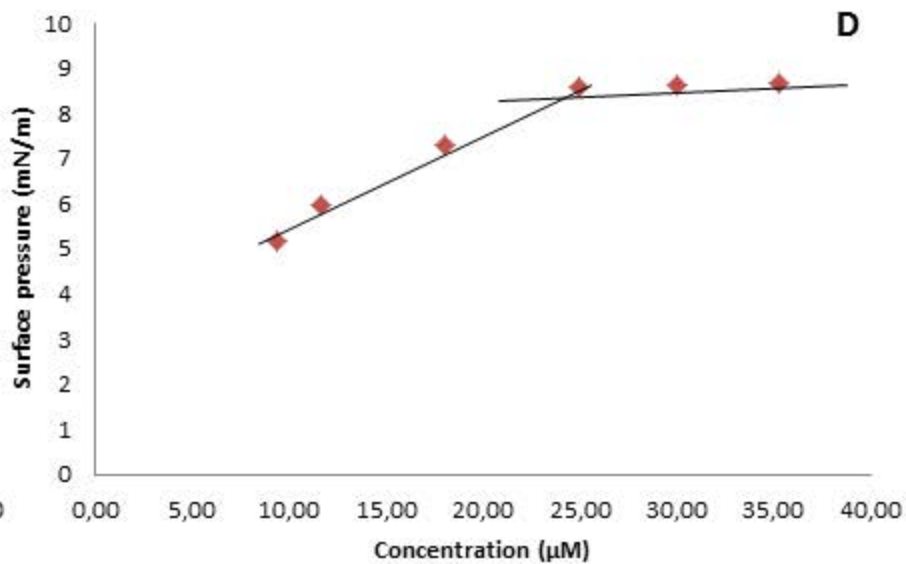
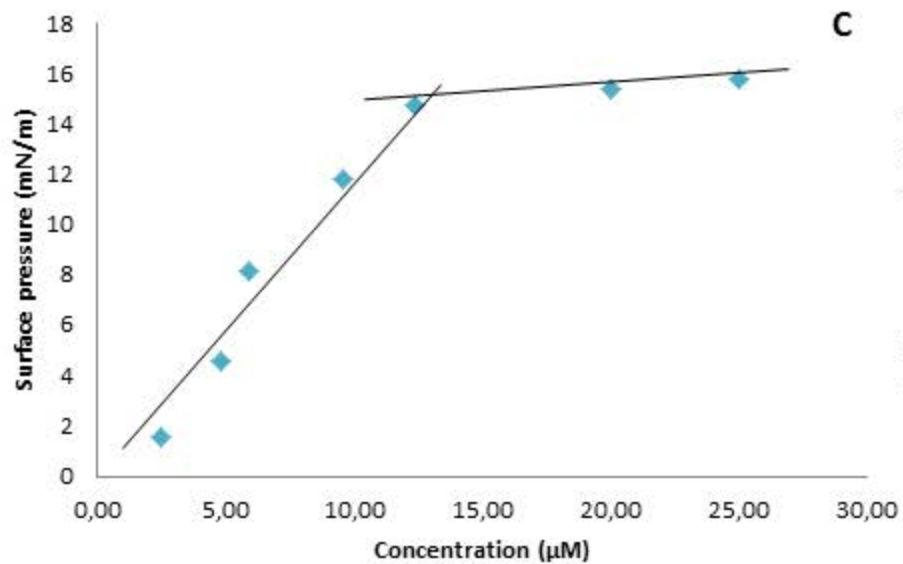
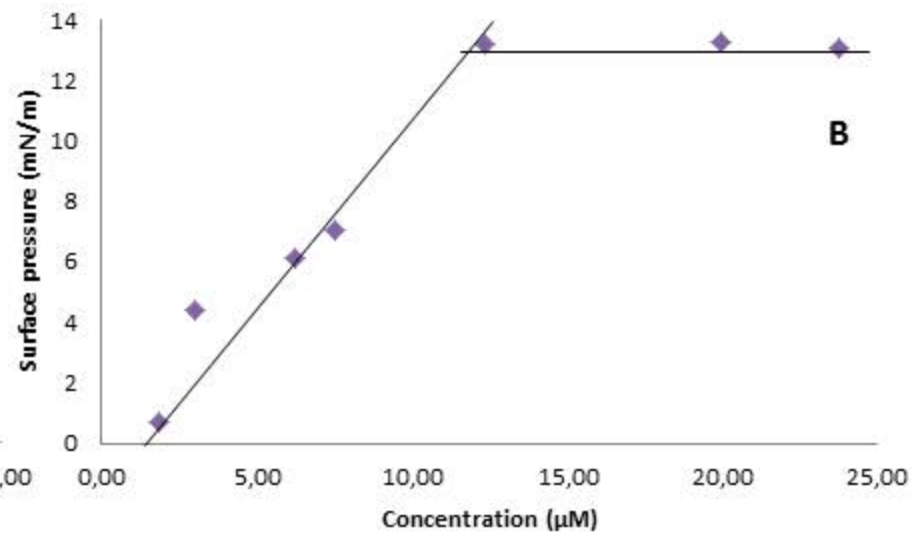
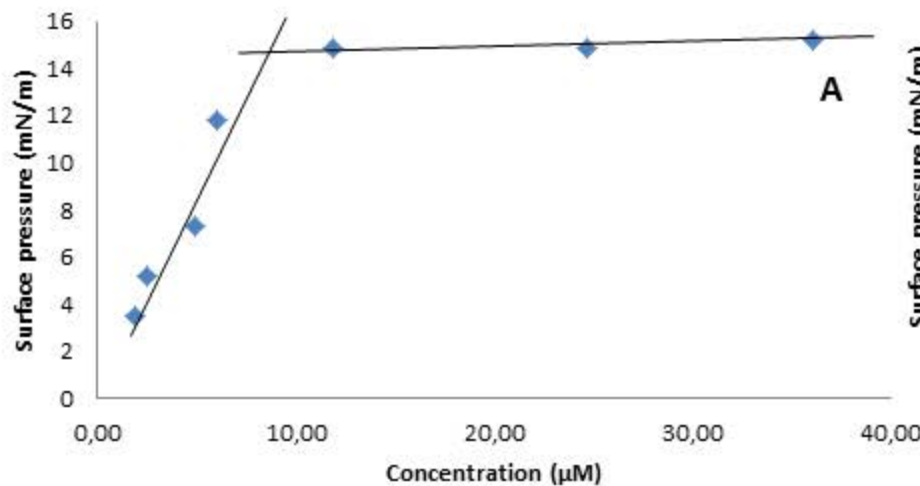


Table 1

	CAC
Xylose monoester (3a)	11.5 ± 1.6 μM
Arabinose monoester (1)	8.4 ± 0.9 μM
Xylose mono- and diesters mixture	23.4 ± 2.3 μM
Arabinose mono- and diester mixture	11.8 ± 0.7 μM