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Abstract

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

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

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

1. Introduction

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

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

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

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

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

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

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

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

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

2. Experimental section

2.1. Materials

2-Methylbutan-2-ol (2M2B, 99%), molecular sieves (4 Å, beads, 8-12 mesh), hexane (>95%), tetrahydrofuran (THF), Novozym 435 (immobilized lipase acrylic resin from *Candida antarctica*, Lot #SLBP0766V), vinyllaurate (>99%), orcinol, chloroform (99%) and D-xylose (>99%) were purchased from Sigma-Aldrich Corp. (St. Louis, USA). L-arabinose, acetic acid (AcOH, >99%), ethylacetate (EA, >99.8%), methanol (>99.9%), petroleum ether (PE, >99.9%) and *n*-butanol (BuOH, >99%) were purchased from Roth (Karlsruhe, Germany). Sulfuric acid (H_2SO_4, 95%) was purchased from VWR (Radnor, USA). Acetonitrile (>99.9%) and propan-2-ol (>99%) were purchased from Carlo Erba Reagents (Dasit Group S.p.A, Cornaredo, Italy).

2.2. Methods

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

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

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

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

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

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

2.2.2. Purification, characterization and quantification of the transesterification products

The production of pentose fatty esters was investigated by TLC, using pre-coated TLC-sheets ALUGRAM® Xtra SIL G/UV_{254} (Macherey-Nagel Gmbh & Co., Düren, Germany) and BuOH : AcOH : water (2/1/1) as the mobile phase. Products were revealed using 0.2 % (w/v) orcinol in H_2SO_4 (20 % v/v in water) and heating at 250 °C.

After removal of enzymes and molecular sieves, 2M2B was evaporated using a rotary evaporator (Büchi Labortechnik AG, Flawil, Switzerland) and crude products with remaining reactants were collected. Two hexane washings were then performed to eliminate the remaining vinyllaurate and a white paste was collected for both D-xylose and L-arabinose-based esters. Vinyllaurate removal was qualitatively assessed by HPLC. Finally, the residual pentose was precipitated in THF (100 mL) leading to soluble fractions containing mono- and diesters collected for further purification. Residual pentose was finally solubilized in water (50 mL) and quantified by HPLC.

The purification of D-xylose or L-arabinose laurate esters was performed by silica gel chromatography (9385 Merck Kieselgel 60, 230–400 mesh, 40–63 µm). Diesters were eluted using PE / EA (7/3, v/v) and monoesters were eluted using pure EA. All the products were obtained as a white crystalline powder.

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

5-*O*-lauryl-L-arabinofuranose 1. White solid, mp 130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): α/β = undetermined ratio, δ 5.30-5.35 (m, H-1α, H-1β), 4.20-4.35 (m, 2 H-5α, 2 H-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 (m, 2H), 1.25-1.35 (m, 16H), 0.90 (t, *J* = 7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.8 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 (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 experiment (HMBC): correlations between C=O and H-5; ESI-MS: 355.2 $(M + Na)^+$; ESI-HRMS : *m/z* calcd for $C_{17}H_{32}O_6Na$ 355.2097, found 355.2089.

3,5-di-*O*-lauryl-L-arabinofuranose 2. White solid, mp 69 °C, ^{1}H NMR (500 MHz, $CDCl_3$) : 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* = 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), 4.13-4.19 (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 (m, 16H), 0.90 (t, *J* = 7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): 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), 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 63.4 (C-5 α and β), 2D experiments (HMBC): correlations between C=O 174.6 and 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* calcd for $C_{29}H_{54}O_7Na$ 537.3767, found 537.3773.

5-*O*-lauryl-D-xylofuranose 3a. White solid, mp 95 °C (lit. 93-95 °C [35]), ^{1}H NMR (600 MHz, CD_3OD): 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* = 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

Hz, H-5β), 4.13-4.18 (m, H-3α, H-5α), 4.05 (dd, *J* = 4 Hz, *J* = 2 Hz, H-3β), 3.96-3.98 (m, H-2β), 3.94 (t, *J* = 4 Hz, H-2α), 2.34 (q, *J* = 7 Hz, 2H), 1.59-1.65 (m, 2H), 1.25-1.35 (m, 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 β), 104.3 (C-1β), 97.8 (C-1α), 82.2 (C-2β), 80.9 (C-4β), 78.2 (C-2α), 77.7 (C-4α), 74.8 and 74.6 (C-3α and β), 65.4 (C-5α), 64.7 (C-5β), 2D experiment (HMBC): correlations between C=O and H-5; ESI-MS: 355.3 $(M + Na)^+$; ESI-HRMS : *m/z* calcd for $C_{17}H_{32}O_6Na$ 355.2097, found 355.2092.

4-*O*-lauryl-D-xylopyranose 3b. White solid, mp 96 °C, ^{1}H NMR (500 MHz, CD_3OD): α/β = 2/1, δ 5.23 (d, *J* = 3 Hz, H-1α), 4.85 (dd, *J* = 8 Hz, *J* = 3 Hz, H-4β), 4.79 (td, *J* = 8 Hz, *J* = 5.5 Hz, H-4α), 4.72 (d, *J* = 6 Hz, H-1β), 4.14 (dd, *J* = 12 Hz, *J* = 5 Hz, H-5β), 3.94 (t, *J* = 8.5 Hz, H-3α), 3.72-3.83 (m, H-3β, 2xH-5α), 3.60 (d, *J* = 8.5 Hz, H-2α), 3.47 (t, *J* = 7 Hz, H-2β), 3.38 (dd, *J* = 12 Hz, *J* = 8.5 Hz, H-5β), 2.34 (q, *J* = 6 Hz, 2H), 1.58-1.65 (m, 2H), 1.25-1.35 (m, 16H), 0.87 (t, *J* = 7 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD): δ 173.7 (C=O α and β), 96.8 (C-1β), 92.4 (C-1α), 73.7 (C-2β), 72.9 (C-3β), 72.6 (C-2α), 71.7 (C-3α), 71.2 (C-4α), 71.1 (C-2β), 62.0 (C-5β), 59.7 (C-5α), 2D experiment (HMBC): correlations between C=O and H-4; ESI-MS: 327.2 $(M + H)^+$, 355.2 $(M + Na)^+$, 385.1 $(M + K)^+$; ESI-HRMS : *m/z* calcd for $C_{17}H_{32}O_6Na$ 355.2097, found 355.2089.

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

4β), 4.17 (dd, *J* = 12 Hz, *J* = 5 Hz, H-5α), 4.14-4.16 (m, H-3β), 2.30-2.39 (m, 4H), 1.58-1.62 (m, 4H), 1.19-1.39 (m, 32H), 0.90 (t, *J* = 7 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 175.0 (C=O β), 174.3 (C=O α), 173.8 (C=O α), 172.8 (C=O β), 100.9 (C-1β), 95.3 (C-1α), 81.1 (C-2β), 80.7 (C-4β), 79.9 (C-2α), 76.7 (C-4α), 74.2 (C-3α), 73.6 (C-3β), 62.6 (C-5β), 62.3 (C-5α), 2D experiment (HMBC): correlations between C=O (175.0 and 174.3) and H-2, and between C=O (173.8 and 172.8) and H-5; ESI-MS: 537.5 $(M + Na)^+$; ESI-HRMS : *m/z* calcd for $C_{29}H_{54}O_7Na$ 537.3767, found 537.3759.

3,5-di-*O*-lauryl-D-xylofuranose 5. White solid, mp 77 °C, ^{1}H NMR (500 MHz, $CDCl_3$): α/β = 1/0.2**,** δ 5.47 (d, *J* = 4 Hz, H-1α), 5.28 (d, *J* = 1 Hz, H-1β), 5.17 (dd, *J* = 5 Hz, *J* = 3 Hz, H-3α), 5.11 (dd, *J* = 5 Hz, *J* = 2 Hz, H-3β), 4.54-4.60 (m, H-4α, H-4β), 4.25-4.33 (m, 2 H-5β), 4.10-4.22 (m,2 H-5α, H-2α, H-2β), 2.25-2.35 (m, 4H), 1.55-1.64 (m, 4H), 1.20-1.28 (m, 32H), 0.80 (t, *J* = 7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.80 (C=O α), 173.7 (C=O β), 173.5 (C=O α and β), 103.1 (C-1β), 96.0 (C-1α), 80.6 (C-2β), 78.6 (C-3α), 78.3 (C-3β), 77.8 (C-4β), 75.7 (C-2α), 75.0 (C-4α), 63.1 (C-5β), 62.2 (C-5α), 2D experiment (HMBC): correlations between C=O (173.8 and 173.5) and H-3, and between C=O (173.7 and 173.5) and H-5; ESI-MS: 537.5 $(M + Na)^+$; ESI-HRMS : *m/z* calcd for $C_{29}H_{54}O_7Na$ 537.3767, found 537.3777.

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

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

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

The quantification of residual sugars was also performed by HPLC using a NUCLEODUR® 100-5 NH_2-RP, 5 µm 250 x 4 mm (Macherey Nagel) column at 40 °C. Pure sugars were used as standards. Sugars were eluted at 1 $mL.min^{-1}$, at 40 °C and with an acetonitrile (A)/water (B) mobile phase 75/25 % in isocratic flow. The detection was performed with a dynamic light scattering detector (PL-ELSD 1000, Polymer Laboratories) at 40 °C under 350 kPa azote pressure. Retention time of D-xylose and L-arabinose were 4.5 and 4.2 minutes respectively.

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

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

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

2.2.4. pH stability investigation

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

3. Results

Transesterification reactions between L-arabinose or D-xylose and vinyllaurate 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 vinyllaurate (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)

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

3.2. Enzymatic synthesis of D-xylose laurate esters

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

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

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

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

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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

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

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

4. Discussion

Numerous studies from literature deal with esterification and transesterification reactions catalysed by lipases for hexoses acylation, mainly D-glucose. In this context, the selective acylation of the primary hydroxyl group for 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

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

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

5. Conclusions

This study dedicated to the lipase-catalysed synthesis of fatty esters from two biomass-derived pentoses, D-xylose and L-arabinose, reports the full characterization of the esters produced and a better understanding of the regioselectivity of the lipase-catalysed transesterification with both pentoses. In this work, the enzymatic synthesis of D-xylose and L-arabinose laurate esters using *C. antarctica* lipase B (N435) as a biocatalyst was reported. Both L-arabinose and D-xylose gave rise to the synthesis of pentose laurate esters as furanose isomers indicating a regioselective first acylation onto the primary hydroxyl group. A second acylation could then occur either selectively on *O*-3 for L-arabinose or as a mixture of diacylated products on *O*-2 and *O*-3 positions for D-xylose. The nature of the pentose influenced kinetics of production and obtained yields. Kinetics of synthesis of D-xylose based esters were slower but yields were higher than those obtained for L-arabinose based esters.
Investigation of surfactant properties of pentoses laurate esters indicated that D-xylose and L-arabinose mono- and diesters exhibited good surfactant properties, such as low CAC, whether purified or in mixtures.

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

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Figures Captions

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

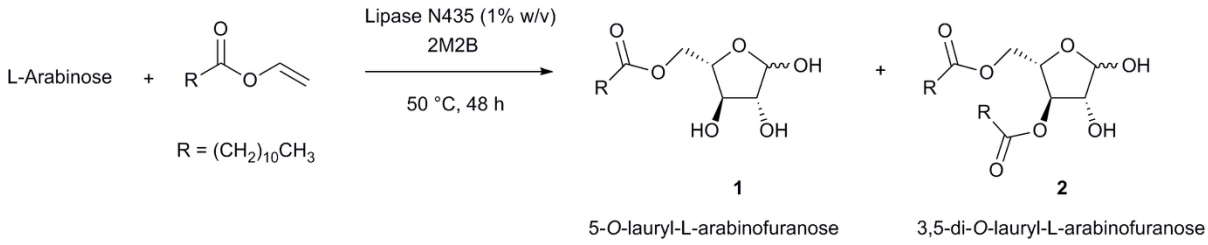
Figure 2. (A) Transesterification reaction of D-xylose and vinyllaurate performed by the lipase Novozym435. (B) Kinetics of synthesis of xylose laurate esters quantified by HPLC. Reactions were performed at 50°C during 48h with 50 mM xylose, 150 mM vinyllaurate, 1% (w/v) lipase. **3a-b**: xylose laurate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

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

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

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

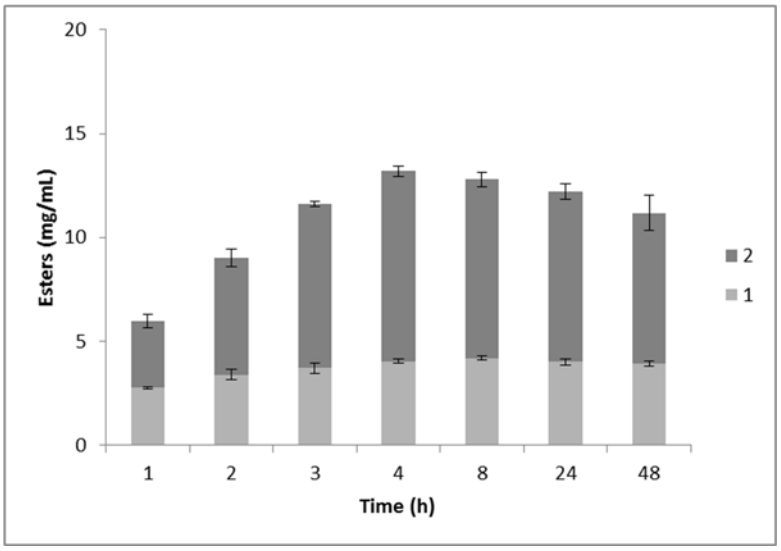
A



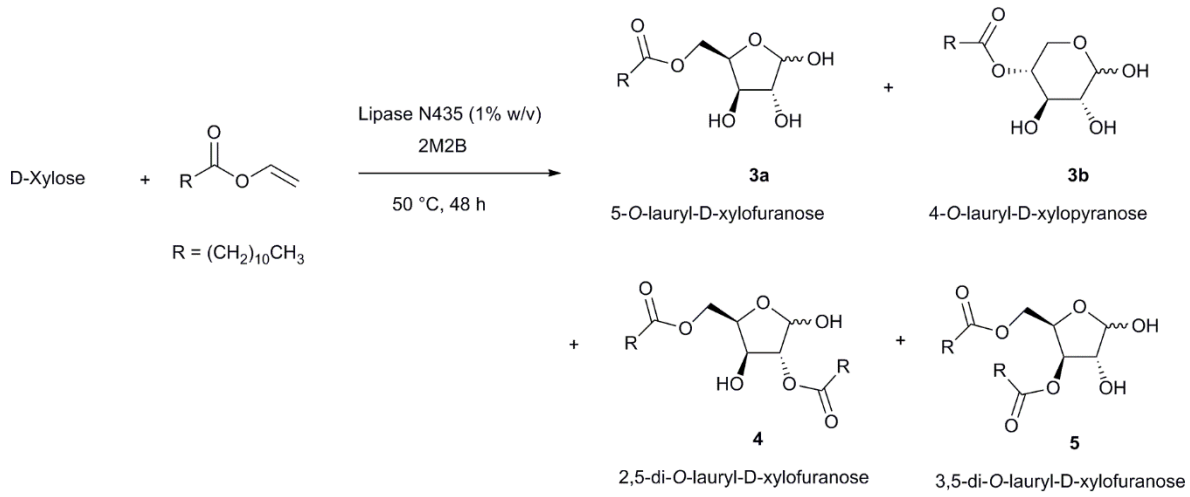
5-*O*-lauryl-L-arabinofuranose

3,5-di-*O*-lauryl-L-arabinofuranose

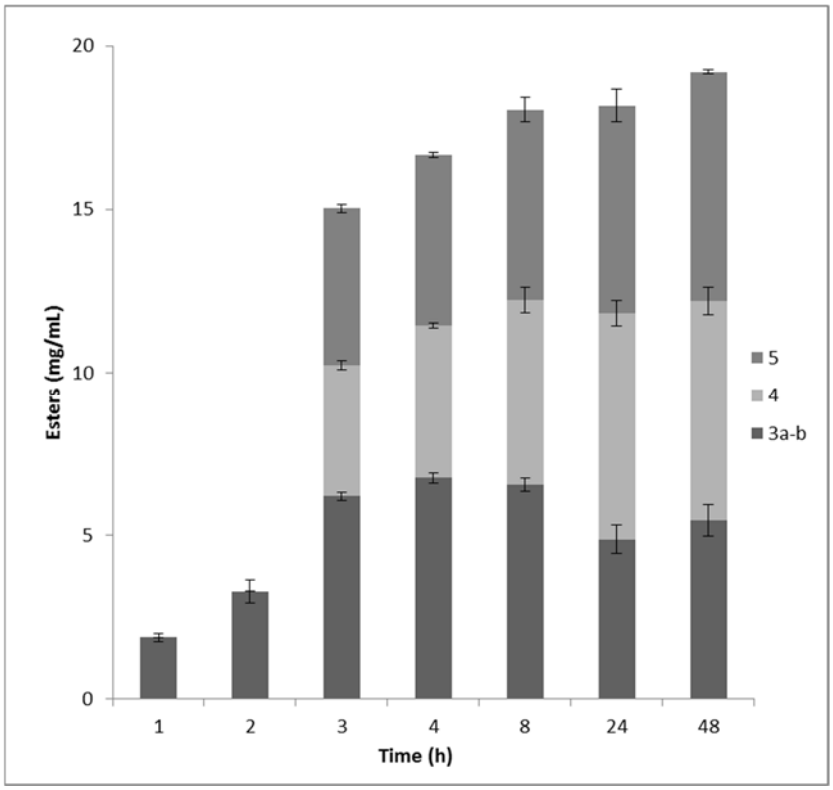
B

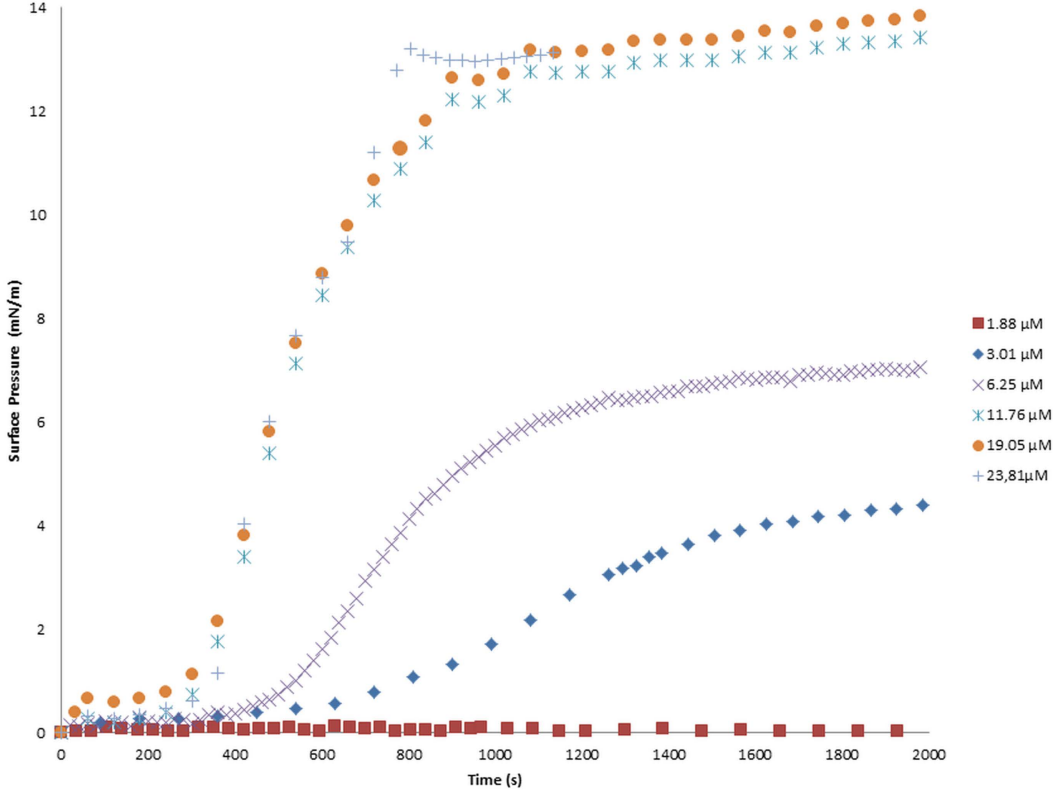


A


D-Xylose
Lipase N435 (1% w/v)
2M2B
50 °C, 48 h
R = (CH2)10CH3
3a
5-O-lauryl-D-xylofuranose
3b
4-O-lauryl-D-xylopyranose
4
2,5-di-O-lauryl-D-xylofuranose
5
3,5-di-O-lauryl-D-xylofuranose

B


Esters (mg/mL)
Time (h)
5
4
3a-b


Surface Pressure (mN/m)
Time (s)
0
2
4
6
8
10
12
14
0
200
400
600
800
1000
1200
1400
1600
1800
2000
1.88 µM
3.01 µM
6.25 µM
11.76 µM
19.05 µM
23,81µM

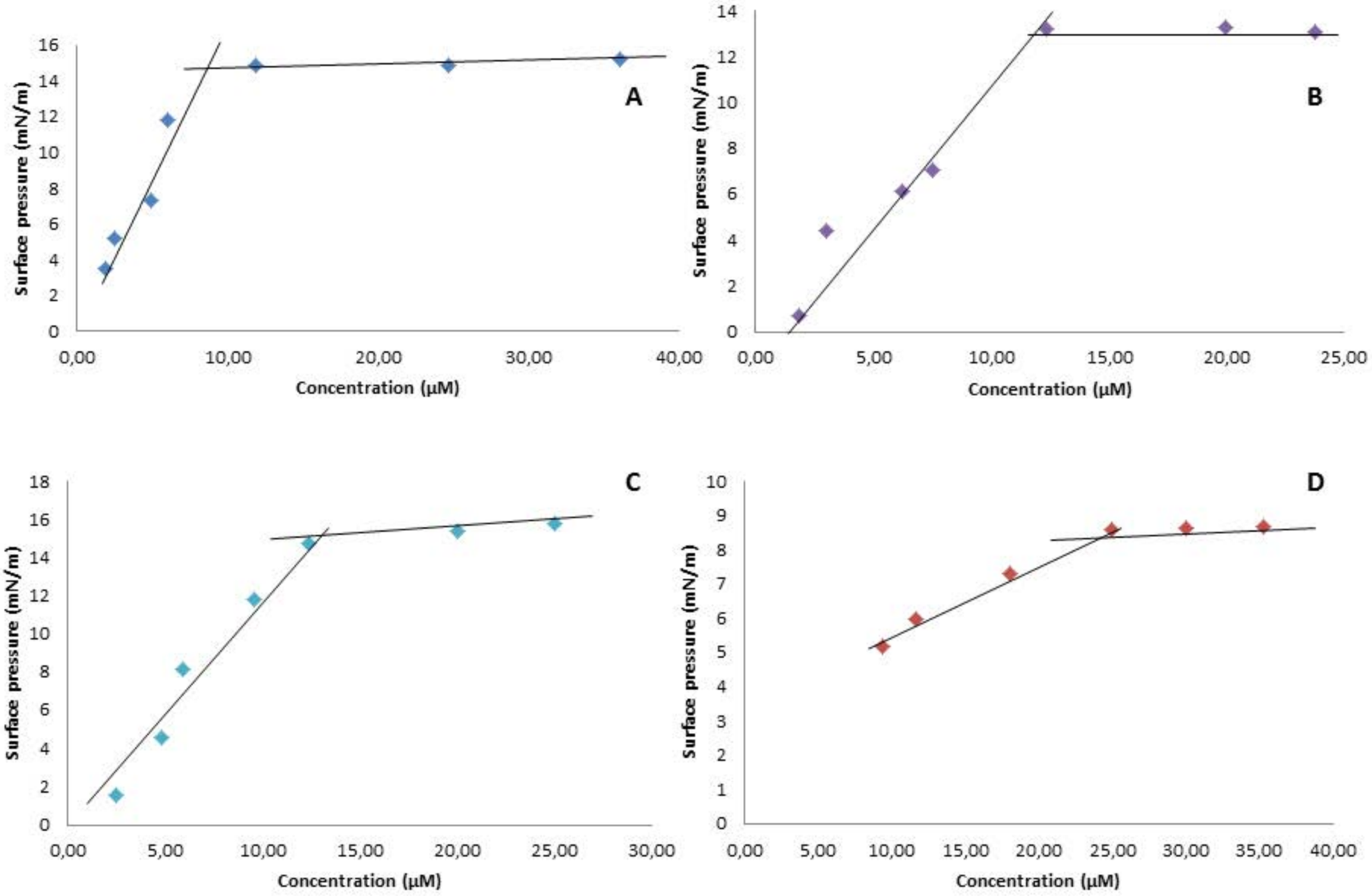

A
Surface pressure (mN/m)
Concentration (µM)
0
2
4
6
8
10
12
14
16
0,00
10,00
20,00
30,00
40,00
B
Surface pressure (mN/m)
Concentration (µM)
0
2
4
6
8
10
12
14
0,00
5,00
10,00
15,00
20,00
25,00
C
Surface pressure (mN/m)
Concentration (µM)
0
2
4
6
8
10
12
14
16
18
0,00
5,00
10,00
15,00
20,00
25,00
30,00
D
Surface pressure (mN/m)
Concentration (µM)
0
1
2
3
4
5
6
7
8
9
10
0,00
5,00
10,00
15,00
20,00
25,00
30,00
35,00
40,00

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