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Note

Neutral pentosides surfactants issued from the butadiene telomerization with pentoses: preparation and amphiphilic properties

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Abstract—Interfacial properties of octadienyl pentosides prepared by the palladium-catalyzed telomerization of butadiene with free pentoses have been evaluated and compared to those of mixtures issued from the autoclaving process.

Keywords: Butadiene telomerization; Octadienyl pentosides; Palladium; Interfacial properties

The progressive changeover of the chemical industry to renewable instead of fossil feedstocks is unavoidable. As far as sustainable development is concerned, there is a need for environmentally friendly surface-active molecules, particularly for pharmaceutical, cosmetics and detergent applications.[1] In addition, particular efforts have to be pursued to transform the entire vegetal material and to favour no-waste oriented agriculture. In this context, the use of cheap and abundant carbohydrates such as raw materials is of great interest,[2] their transformation into biodegradable surfactants being among the numerous possibilities for their valorization. Although alkylpolyglycosides constitute a class of successfully developed surfactants,[3] some other compounds should also be valuable.[4] For example, neutral amphiphilic molecules could be prepared by grafting one lipophilic chain on a free carbohydrate. The palladium-catalyzed telomerization of butadiene with sugars corresponds to a 100% atom economical reaction, which allows their direct transformation into the target through the grafting of an octadienyl chain as the lipophilic moiety.[5,6] For several years, we have been involved in a research program dedicated to the valorization of pentoses now readily accessible from wheat straw and bran.[7] Starting from such polyfunctional nucleophiles as telogens, some of our efforts have been directed to the control of the degree of substitution.

Selective functionalization with one or more C-8 alkenyl chains opens a direct way from a given carbohydrate to surfactants having different hydrophilic–lipophilic balances, and thus to a wide range of applications. We already described conditions in both organic[8,9] and aqueous media,[10] which allowed a direct access to the major mono- or dioctadienyl xylosides and arabinosides (Scheme 1), and demonstrated that the presence of a tertiary amine was not required for high sugar concentrations in DMF.[12]

In order to decrease the number of isomers, successful reactions have also been carried out starting from triacetylated[11] or tribenzylated[13] pentoses. Having in hand selective routes to synthesize octadienyl pentosides, the evaluation of their surface-active properties has been carried out. We present here the characterization of

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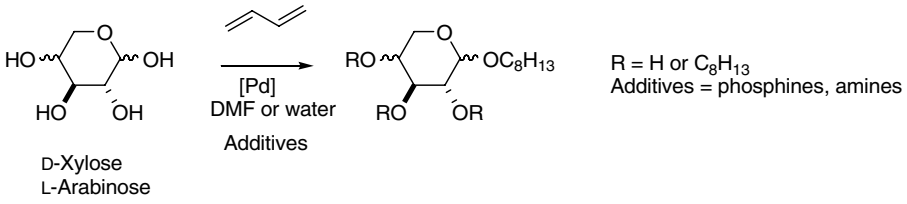


Scheme 1. Synthetic strategy for the preparation of mono- or polyoctadienyl pentosides.[8,10]

the major isolated pentosides together with their interfacial properties as compared to the interfacial properties of mixtures directly issued from the autoclaving process after getting butadiene dimers and residual metal.

Following the above mentioned telomerization experiments,[8–11] we were able to prepare and isolate monooctadienyl pentosides in pure forms **1**–**3** or in admixture with dioctadienyl pentosides **4**–**6** (Scheme 2).

The major monooctadienyl pentosides ethers, namely 2-(*E*)-7-octadienyl β-D-xylopyranoside **1**, 2-(*E*)-7-octadienyl α-D-xylopyranoside **2** and 2-(*E*)-7-octadienyl α-L-arabinopyranoside **3**, have been isolated in sufficient amount to determine their surface-active properties.

The surface tension variations as a function of concentration of the major isolated pentosides **1**, **2** and **3** are plotted in Graph 1, which evidences the marked surface activity of these molecules. The critical micellar concentration (CMC) values as well as the surface tensions at CMC and minimum areas per molecule are collected in Table 1 (entries 1–3).

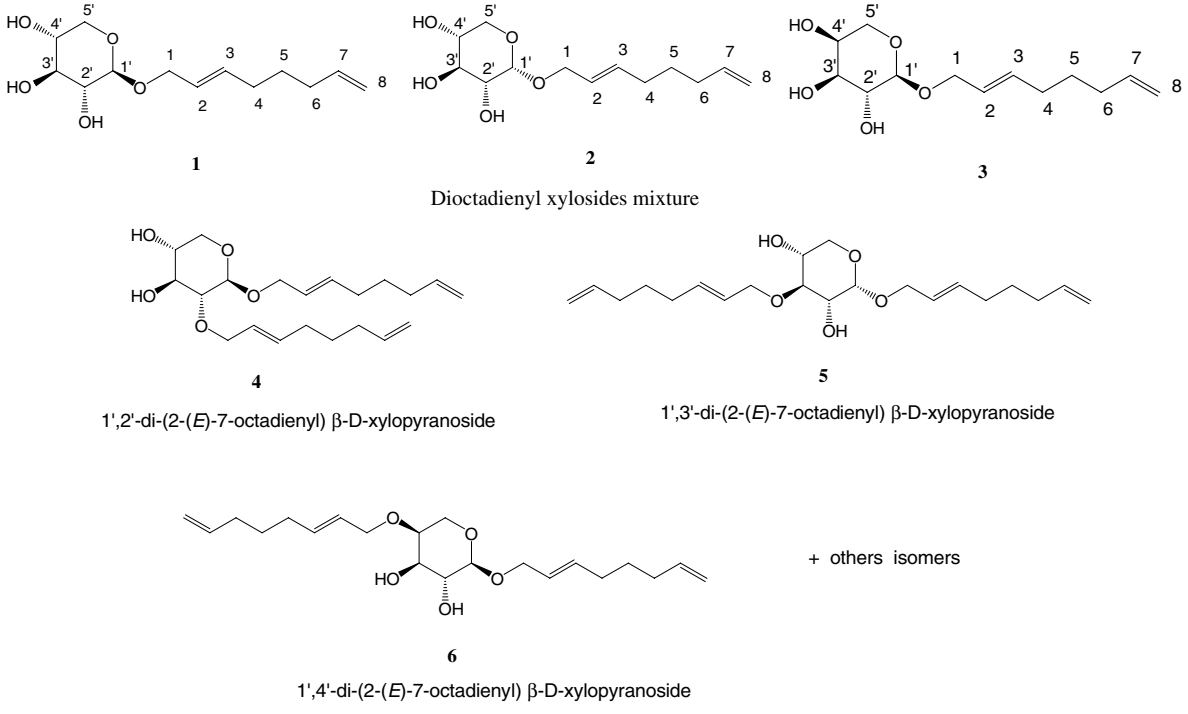
The minimum area per molecule $a_{\min}$ was calculated from the slope of the surface tension curve at the CMC using Gibbs Eq. 1:

$$\alpha_{\mu\nu} = \left(\frac{1}{N_A \Gamma_0}\right) \quad \text{with } \Gamma_0 = -\frac{1}{PT}\left(\frac{\delta\gamma}{\delta \Lambda v X}\right)_{X\to XMX} \qquad (1)$$

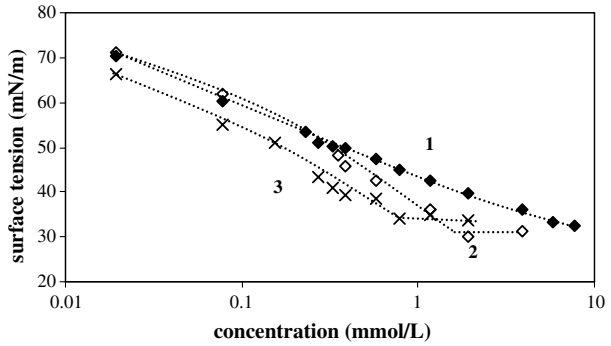
N_A is the Avogadro number.

No CMC was detected for 2-(*E*)-7-octadienyl β-D-xylopyranoside **1**, the solution becoming turbid above 1000 mg/L (3.88 mmol/L), while a CMC of 500 mg/L (1.94 mmol/L) was observed for the 2-(*E*)-7-octadienyl α-D-xylopyranoside **2** (Table 1, entries 1 and 2). In addition, similarly to alkyl glucosides,[14] the α-anomers showed stronger surface activity than the β-anomers (Table 1, entry 2 vs 1). These observations are in accordance with the fact that among the alkyl glucosides, α-anomers are less hydrophilic than β-anomers,[14] involving different thermotropic properties.[15]

Differences in head group conformation also have a strong effect on surface activity, as shown by the lower



Scheme 2. Monooctadienyl xylosides and arabinoside obtained in pure forms and the mixture of dioctadienyl xylosides.



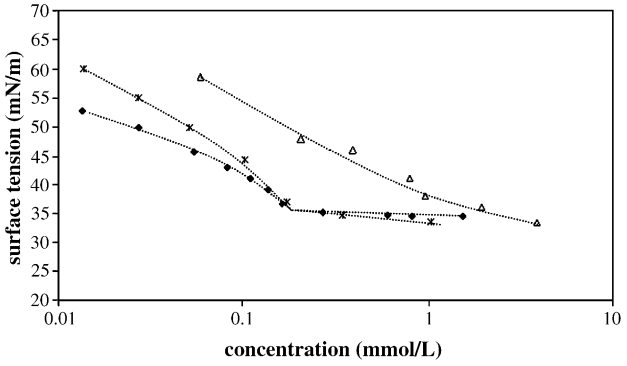
Graph 1. Surface tension of isolated pentosides as a function of concentration: (♦) octadienyl β-D-xylopyranoside **1**; (◇) octadienyl α-D-xylopyranoside **2**; (×) octadienyl α-L-arabinopyranoside **3**.

CMC of the 2-(*E*)-7-octadienyl α-D-arabinopyranoside **3** compared to the 2-(*E*)-7-octadienyl α-D-xylopyranoside **2** (Table 1, entry 3 vs 2). It seems that the position equatorial or axial of the OH group at C-4′ has a great importance. The conformation of the sugar head groups and their degree of hydration generally strongly influence the way the head groups will pack and how easy the formation of micelles will take place, and thus may strongly influence the CMC value.[16] CMC values obtained for all the compounds studied are also significantly lower than the values obtained with octyl glucosides (C_8Glc) (12 and 20 mmol/L for C_8αGlc and C_8βGlc, respectively).[14] These lower values could be due to the presence of only 3 OH groups on the polar head for the pentosides compared to 4 for the glucosides. These low CMC values were observed despite the presence of an unsaturation in the chain, which led sometimes to an increase of the CMC values as observed in the case of sodium carboxylates surfactants bearing a double bond in the middle[17] or on the terminal position of the hydrocarbon chain[18] and in other glucose based surfactants.[19]

Regarding the molecular area at the interface, the values obtained for the α-anomers (Table 1, entries 2 and 3) are slightly lower but of the same order of magnitude as those obtained for glucose derivatives (i.e., 47 Å^2/molecule for C_8αGlc[14]). These properties were compared with those of the mixtures of monooctadienyl xylosides (Table 1, entry 4), dioctadienyl xylosides (entry 5) and a crude mixture directly issued from the autoclave (entry 6). A monooctadienyl xylosides mixture containing 90% 2-(*E*)-7-octadienyl β-D-xylopyranoside **1** and 10% 2-(*E*)-7-octadienyl α-D-xylopyranoside **2** (% evaluated by GC) behaves in a similar manner as compared to **1** alone and does not display a sharp CMC value (Graph 2 and Table 1, entry 4). This mixture exhibits a surface tension of 33.5 mN/m lower than that of pure **1** due to the presence of the α-anomer.

The surface activity of a complex mixture of isomers of dioctadienyl xylosides was then evaluated. A surface tension of 35 mN/m at a CMC of 70 mg/L (0.19 mmol/L) was measured and a molecular area at the interface of 57.5 Å^2 calculated (Table 1, entry 5). When compared to the dioctadienyl xyloside mixture, these values (CMC, γ and a_{min}) are in complete accordance with the presence of a supplementary octadienyl hydrophobic chain in the molecule.

Finally, to complete our study, we determined the surface tension behaviour of a crude mixture directly issued from the autoclaving process after evaporation of the solvent, the butadiene dimers and filtration of the palladium species. This mixture contains 6% nonreacted xylose, 62% monooctadienyl xylosides, 27% dioctadienyl xylosides and 5% dioctadienyl xylosides and the overall



Graph 2. Surface tension of the telomer mixtures: (△) monooctadienyl xylosides (**1**+**2**); (♦) dioctadienyl xylosides mixture; (∗) crude mixture.

Table 1. Surfactant properties of mono- and di-octadienyl ethers and mixtures

Entry	Compounds	CMC		γ_{CMC} (mN/m)	a_{min} (Å^2/molecule)
		(mg/L)	(mmol/L)		
1	2-(*E*)-7-Octadienyl β-D-xylopyranoside **1**	—	—	36[a]	—
2	2-(*E*)-7-Octadienyl α-D-xylopyranoside **2**	500	1.94	31	41.5
3	2-(*E*)-7-Octadienyl α-L-arabinopyranoside **3**	180	0.70	34	43.0
4	Monooctadienyl xylosides (90% **1**, 10 % **2**)	—	—	33.5[b]	—
5	Dioctadienyl xylosides mixture	70	0.19	35	57.5
6	Crude mixture of xylosyl telomers[c]	55	0.19	35	—

[a] Above 1000 mg/L the value of surface tension tends to slowly decrease but the solution becomes turbid, so that the existence of a true CMC is questionable.

[b] Surface tension and area determined at a concentration of 1 mmol/L.

[c] Composition of the crude mixture: 6% xylose, 62% monooctadienyl xylosides, 27% dioctadienyl xylosides, 5% trioctadienyl xylosides (composition evaluated by GC).

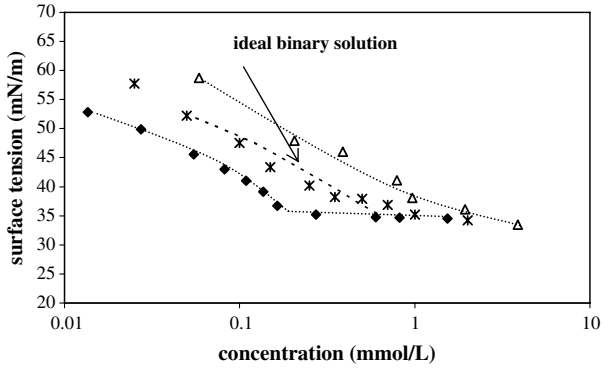
surfactant molar concentration was calculated by taking into account the fraction of each compound. This crude mixture exhibits a surface tension of 35 mN/m at a CMC of 55 mg/L (0.19 mmol) (Table 1, entry 6).

From Graph 2, it appears that the CMC of the crude mixture (expressed in mmol/L) is equal to the CMC of the dioctadienyl xylosides although 62% of monooctadienyl xylosides are present. This effect could be explained either by a synergism in the surface properties of the dioctadienyl xylosides and monooctadienyl xylosides molecules or by the surface activity of a minor component, as trioctadienyl xylosides. Indeed, Castro et al.[20] showed that synergistic effects for C_{12}–C_{14} alkyl glucosides could influence the surfactant properties of mixtures of these glucosides. In order to study this hypothesis, we prepared a mixture of mono- and dioctadienyl xylosides containing the same relative molar fraction as the crude mixture (70% monooctadienyl xylosides and 30% dioctadienyl xylosides). We compared its surface tension variations with those of di- and monooctadienyl xylosides alone (Graph 3).

We plotted on the same graph the result expected for an ideal mixture, for which no synergism occurs. In that case, the overall surfactant concentration C^0 required to lower the surface tension to a certain value γ is given by Eq. 2:[21]

$$\frac{1}{C^0} = \frac{\alpha}{C^0_A} + \frac{1-\alpha}{C^0_B} \quad (2)$$

where C^0_A and C^0_B are the concentrations of pure surfactants A and B required to produce the fixed value of surface tension and α is the molar fraction of surfactant A. The model rigorously applies to a real binary solution, whereas a much more complex mixture of isomers is present here. Nevertheless, Graph 3 shows that the surface tension variations of the reconstituted binary mixture are very close to what is expected for an ideal mixture. Therefore, no significant synergism is revealed.



Graph 3. Surface tension of a binary mixture of xylosyl mono- and dioctadienyl ethers as a function of concentration by comparison to an ideal binary solution shown by the dotted line: (△) monooctadienyl xylosides (**1**+**2**); (♦) dioctadienyl xylosides mixture; (∗) reconstituted mixture; (----) variation expected for an ideal binary solution of the same molar composition as the reconstituted mixture.

However, the variations observed with the crude mixture (Graph 2) are shifted towards lower concentrations, suggesting the important role of another component, possibly the xylosyl trioctadienyl ethers, in the observed surface activity. These results illustrate the good surface-active character of the crude mixture of xylosyl octadienyl ethers and indicate that the tedious separation of pure isomers is not necessary.

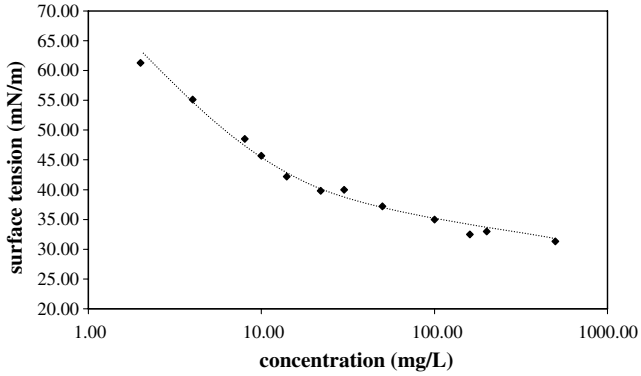
As mentioned in the Introduction, pentoses are readily accessible from wheat straw and bran.[7] So, we have carried out the telomerization of butadiene with a bran syrup having the composition given in Table 2.

The crude mixture then obtained containing 1% bran syrup, 67% monooctadienyl glucosides, 31% dioctadienyl glucosides and 1% trioctadienyl glucosides was evaluated. The curve in Graph 4 revealed satisfactory surface-active behaviour of this crude mixture although no sharp value of CMC could be determined, as it can happen with complex mixtures. Continuous decrease of surface tension down to values around 30–35 mN/m was observed over a long range of concentrations.

In conclusion, the palladium-catalyzed telomerization of butadiene with pentoses or bran syrup results to mono- or polyoctadienyl pentosides. Thorough separations of the major resulting products are performed leading to pure monooctadienyl xylosides or arabinosides. The study of their surface activity showed their interesting capacity of lowering surface tension down to 30–35 mN/m at relatively low concentrations in the range of 1–4 mmol/L. Submitting crude mixtures of

Table 2. Composition of the bran syrup used for the butadiene telomerization

Dry material (DM)	72.6%
L-Arabinose/DM	33.5%
D-Xylose/DM	54.2%
D-Glucose/DM	8.9%
D-Galactose+D-mannose/DM	1.7%
Polysaccharides/DM	1.2%
Purity	99.5%



Graph 4. Surface tension of a crude telomer mixture issued from the telomerization of butadiene with bran syrup as a function of concentration.

telomers of xylose or bran syrup to the same screening established that the surface activity was not improved after the separation process. Therefore, for an industrial application of these surfactants, the use of the lower cost, crude mixtures can be recommended.

1. Experimental

1.1. General methods

^1H and ^{13}C NMR were recorded in D_2O on a Bruker AC250 spectrometer (^1H, 250 MHz; ^{13}C, 63.8 MHz) and referenced to TMS. IR analyses were recorded on a Spectrafile IR-TF plus Midac as films. HR-MS analyses were performed on a Q-TOF micro (Micromass) with an electrospray source (injection: 5 μL/min, solvent: MeOH+0.2% (vol) HCOOH, source temperature: 80 °C, drying gas: N_2, 100 °C).

GC analyses of acetylated telomers were recorded on a Hewlett–Packard HP-6890 gas chromatograph, fitted with DB-1 capillary column (25 m, 0.32 mm), a flame ionization detector and HP-3395 integrator under the following conditions: helium as vector gas (5×10^4 Pa), temperature of injector: 250 °C, temperature of the oven: isotherm 150 °C, 5 min, then 150–300 °C (10 °C/min) and isotherm 300 °C, 5 min.

TLC are carried out on SDS Silica 60 (40–63 μm), Art 2050044. Separations of telomer forms were performed on normal silica (63–200 μm), 9:1 petroleum ether–EtOAc.

Solvents, substrates L-arabinose, D-xylose, triphenylphosphine and Pd(II) catalyst were commercially available (Aldrich, Acros or Strem Chemicals) and used as received. $Pd_2(dba)_3{\cdot}CHCl_3$ was prepared following a reported procedure.[22] Butadiene N25 from Air Liquide (Paris) was used without purification. Bran syrup was obtained from Agro Industrie Recherches Développements (ARD, F-51110 Pomacle) and used as received.

Surface tension was measured by the Wilhelmy plate method. Aqueous solutions were prepared by dissolving the samples in ultra-pure deionized water (18 MΩ cm^{-1}) and diluting to the desired concentration. All measurements were performed at 25 °C with an automatic tensiometer (Krüss K100). Surface tension measurements were repeated three times. The time required for equilibrium was fixed to 30 min.

1.2. General procedure for the purification of octadienyl pentosides 1–3 as their acetylated derivatives

Telomerization was carried out on 3 g of pentoses (D-xylose or L-arabinose or bran syrup) as previously described.[8] In the following is pointed out a simple separation procedure of monooctadienyl pentosides from crude autoclaving mixture without chromatography steps. Next, octadienyl pentosides **1**–**3** have been isolated as their acetylated derivatives after laborious chromatographies.

After cooling the autoclave, the remaining butadiene, volatile dimers and solvent were condensed in a Schlenk tube and the residual mixture contained the nonreacted pentose and its octadienyl derivatives. An aliquot was acetylated with an excess of Ac_2O–Py 1:1 for 2 h at 50 °C and analyzed by GC. Diethyl ether (50 mL for 1 g of starting pentose) was then added to the residual mixture to precipitate the residual pentose. After evaporation of the solvent, the residue was dissolved in 1:10 water–pentane (440 mL always for 1 g pentose used in the telomerization process). Separation of the two phases led to an organic phase containing the polyoctadienyl pentosides and an aqueous one containing the monooctadienyl ones.

After evaporation of the aqueous phase, the monooctadienyl pentosides were acetylated with acetic anhydride (10 mL) and NaOAc (0.5 g) (for 1 g pentose used in the telomerization process) at 50 °C for 2 h. Ethyl acetate (50 mL) was added to the resulting mixture and the excess of acid was removed by washing with a saturated NaOAc solution (5×100 mL). After drying over $MgSO_4$, the organic phase was concentrated under diminished pressure and the mixture was purified by chromatography on silica gel of acetylated monooctadienyl pentosides (9:1 petroleum ether–AcOEt).

The separation of the mixture of acetylated monooctadienyl xylosides (1.1 g) was carried out very slowly (over 5 days) and led, respectively, to 2-(*E*)-7-octadienyl 2′,3′,4′-tri-*O*-acetyl-β-D-xylopyranoside (357 mg, 32%) and 2-(*E*)-7-octadienyl 2′,3′,4′-tri-*O*-acetyl-α-D-xylopyranoside (132 mg, 11%). In the same way, separation of a mixture of acetylated monooctadienyl arabinosides (1.4 g) led to pure 2-(*E*)-7-octadienyl 2′,3′,4′-tri-*O*-acetyl-α-L-arabinopyranoside (197 mg, 11%).

These acetylated monooctadienyl pentosides are deprotected before measuring surfactant properties.

1.2.1. General procedure of deprotection of acetylated monooctadienyl pentosides. Acetylated monooctadienyl pentosides were dissolved in 1:1 MeOH–CH_2Cl_2 mixture. A methanolic 0.5 M solution of NaOMe (1.5 equiv) was slowly added and the reaction followed by TLC using 9:1 CH_2Cl_2–MeOH. After total deprotection, the excess of base was neutralized by adding Amberlite IR-120 resin to obtain neutral pH. The resin was then filtered and washed with MeOH (4×10 mL). The evaporation of the solvent led to the octadienyl pentosides.

1.3. 2-(*E*)-7-Octadienyl β-D-xylopyranoside (1)

From 2-(*E*)-7-octadienyl 2′,3′,4′-tri-*O*-acetyl-β-D-xylopyranoside (302 mg) in MeOH–CH_2Cl_2 (8 mL) and a

methanolic soln of NaOMe (2.4 mL); 191 mg (94%); clear yellow paste; $[\alpha]_D^{20}$ −25 (*c* 0.96, MeOH). IR film (cm^{-1}): 3374 (F), 2927 (m), 2857 (m), 1596 (F), 1416 (m), 1352 (m), 1046 (m). ^1H NMR: δ (ppm) 5.80–5.55 (2H, H-3, H-7), 5.55–5.45 (1H, H-2), 4.95–4.80 (2H, dd, $J_{8a-7} = 1.9$ Hz, $J_{8a-8b} = 18.9$ Hz, H-8), 4.20–4.10 (2H, H-1′, H-1b), 3.95 (1H, dd, $J_{1a-1b} = 11.8$ Hz, $J_{1a-2} = 6.7$ Hz, H-1a), 3.75 (1H, dd, $J_{5'a-5'e} = 11.3$ Hz, $J_{5'e-4'} = 5.2$ Hz, H-5′e), 3.45–3.30 (1H, H-4′), 3.25–3.15 (1H, H-3′), 3.15–3.00 (2H, H-2′, H-5′a), 2.05–1.90 (4H, H-4, H-6), 1.39 (2H, qt, $J_{5-4} = J_{5-6} = 7.5$ Hz, H-5). ^{13}C NMR: δ (ppm) 140.1 (C-7), 136.1 (C-3), 127.9 (C-2), 115.5 (C-8), 104.1 (C-1′), 78.1 (C-3′), 75.2 (C-2′), 71.6 (C-4′), 71.3 (C-1), 69.2 (C-5′), 34.7 and 31.1 (C-4 or C-6), 29.9 (C-5). HRMS: calcd [M+Na] = 281.1365 g/mol; found [M+Na] = 281.1369 g/mol. Anal. Calcd for $C_{13}H_{22}O_5 \cdot 0.5H_2O$: C, 58.43; H, 8.61. Found: C, 58.90; H, 9.19.

1.4. 2-(*E*)-7-Octadienyl α-D-xylopyranoside (2)

From 2-(*E*)-7-octadienyl 2′,3′,4′-tri-*O*-acetyl-α-D-xylopyranoside (471 mg) in MeOH–CH_2Cl_2 (8 mL) and a methanolic soln of NaOMe (3.7 mL); 307 mg (97%); clear yellow paste; $[\alpha]_D^{20}$ +82 (*c* 1.42, MeOH). IR film (cm^{-1}): 3354 (F), 2925 (m), 2860 (m), 1614 (m), 1437 (m), 1352 (m), 1043 (m). ^1H NMR: δ (ppm) 5.80–5.60 (2H, H-3, H-7), 5.61–5.54 (1H, H-2), 4.95–4.75 (2H, H-8), 4.65 (1H, d, $J_{1'-2'} = 3.2$ Hz, H-1′), 4.05 (1H, dd, $J_{1a-1b} = 11.6$ Hz, $J_{1a-2} = 5.1$ Hz, H-1a), 3.85 (1H, dd, $J_{5'a-5'e} = 11.9$ Hz, $J_{5'e-4'} = 6.7$ Hz, H-5′e), 3.55–3.15 (5H, H-1b, H-2′, H-3′, H-4′, H-5′a), 2.15–1.95 (4H, H-4, H-6), 1.40 (2H, qt, $J_{5-4} = J_{5-6} = 7.6$ Hz, H-5). ^{13}C NMR: δ (ppm) 138.6 (C-7), 134.5 (C-3), 126.2 (C-2), 114.0 (C-8), 97.9 (C-1′), 73.9 (C-3′), 72.3 (C-2′), 70.3 (C-4′), 68.0 (C-1), 62.0 (C-5′), 33.1 and 31.6 (C-4 or C-6), 28.4 (C-5′). HRMS: calcd [M+Na] = 281.1365 g/mol, found [M+Na] = 281.1360 g/mol. Anal. Calcd for $C_{13}H_{22}O_5 \cdot 0.5H_2O$: C, 58.43; H, 8.61. Found: C, 58.66; H, 9.09.

1.5. 2-(*E*)-7-Octadienyl α-L-arabinopyranoside (3)

From 2-(*E*)-7-octadienyl 2′,3′,4′-tri-*O*-acetyl-α-D-arabinopyranoside (356 mg) in a MeOH–CH_2Cl_2 (8 mL) and a methanolic soln of NaOMe (2.8 mL); 215 mg (97%); clear yellow paste; $[\alpha]_D^{20}$ −3 (*c* 1.16, MeOH). IR film (cm^{-1}): 3387 (F), 2925 (m), 2853 (m), 1599 (F), 1351 (m), 1088 (m). ^1H NMR: δ (ppm) 5.85–5.75 (1H, H-7), 5.71 (1H, t, $J_{2-3} = 13.8$ Hz, $J_{3-4} = 6.9$ Hz, H-3), 5.59 (1H, dt, $J_{2-3} = 12.5$ Hz, $J_{1b-2} = 5.9$ Hz, H-2), 5.02–4.95 (2H, H-8), 4.25 (2H, dd, $J_{1a-1b} = 12.5$ Hz, $J_{1b-2} = 6.6$ Hz, H-1′, H-1b), 4.10 (1H, dd, $J_{1a-1b} = 12.2$ Hz, $J_{1a-2} = 6.9$ Hz, H-1a), 3.87–3.83 (2H, dd, $J_{5'b-5'a} = 12.5$ Hz, $J_{5'b-4'} = 2.96$ Hz, H-5′b), 3.77–3.72 (1H, H-4′), 3.59–3.48 (3H, H-5′a, H-3′, H-2′), 2.05 (4H, m, H-4, H-6), 1.47 (2H, qt, $J_{5-4} = J_{5-6} = 7.9$ Hz, H-5). ^{13}C NMR: δ (ppm) 138.6 (C-7), 134.5 (C-3), 126.4 (C-2), 113.9 (C-8), 102.4 (C-1′), 73.0 (C-3′), 71.2 (C-2′), 69.5 (C-1), 68.4 (C-4′), 65.7 (C-5′), 33.1 and 31.5 (C-4 or C-6), 28.4 (C-5). HRMS: calcd [M+Na] = 281.1365, found [M+Na] = 281,1373. Anal. Calcd for $C_{13}H_{22}O_5 \cdot 0.5H_2O$: C, 58.43; H, 8.61. Found: C, 58.79; H, 9.17.

1.6. Dioctadienyl xylosides

From the mixture of dioctadienyl xylosides (350 mg) in MeOH–CH_2Cl_2 (8 mL) and a methanolic soln of NaOMe (1.8 mL); 280 mg (98%); yellow oil. Anal. Calcd for $C_{21}H_{34}O_5 \cdot 0.25H_2O$: C, 68.01; H, 9.31. Found: C, 68.32; H, 9.53.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2006.04.023.

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