Palladium-catalysed telomerization of butadiene with aldoses: A convenient route to non-ionic surfactants based on controlled reactions

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Abstract

Palladium-catalysed telomerization of butadiene with aldoses in an organic medium can be directed towards the formation of mono- or di-octadienyl ethers. The relative reactant ratios and the amounts of dissolved gaseous butadiene have been defined as the crucial parameters to this purpose. The resulting octadienyl ethers could be hydrogenated, leading to the corresponding saturated non-ionic surfactants.
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Alkyl glycosides are non-ionic biodegradable surfactants based on renewable carbohydrate raw materials [1,2]. Their specific properties have attracted a considerable industrial interest due to their wide range of applications. In addition to their potential biological and pharmaceutical applications, alkyl glycosides stabilise microemulsions and have been incorporated in detergents, cleaners or cosmetics [1,3]. These compounds have been manufactured in commercial quantities since the late 1970's and their production has increased remarkably in the last decades. Among the different preparation methods used [4], Fischer glycosylation [5] is the oldest and the most current. However, limited yields, combined with the necessity of a trans-glycosylation step, has stimulated a search for alternative approaches to these compounds. The Pd-catalysed telomerization of butadiene with sugars is an elegant way to prepare this type of surfactant in a one pot, 100% atom economical reaction, and has provoked great interest from both an academic [6–9] and an industrial point of view [10–12]. However, carbohydrates are polyfunctional nucleophiles and their reactions can lead to complicated mix-

tures of polyethers having a different number of octadienyl chains.

The control of the degree of sugar etherification has a great importance since it opens a direct way from a given carbohydrate to surfactants having different hydrophilic–lipophilic balances (HLB), and thus to a wide range of applications. The selective introduction of one octadienyl chain is well controlled starting with nucleophiles, such as ammonia [13] aminoalcohols [14] and diols [14–17]. On the contrary, with sugar substrates, high conversion gives a high average degree of etherification (N) by octadienyl chains. Indeed, in the presence of a Pd(II)/PPh$_3$ catalytic precursor in 2-propanol/water as solvent, the reaction of D-glucose and sucrose with butadiene affords a mixture of octadienyl ethers with $N = 2.5$ and 5.5, respectively at 95% conversion [10]. With sucrose, the N value decreases to 4.4 (at 88% conversion) when the reaction is carried out under constant butadiene pressure [11,18]. Using a Pd(II)/TPPTS catalytic precursor in iso-propanol/water, the N decreases to 1.3 [6] or 1.2 [7].

We have recently reported that the reaction of aldopentoses (D-xylose and L-arabinose) with butadiene led to the predominant formation of monoethers (62% monoethers, 97% conversion) when carried out in DMF in the presence of Pd(II) and phosphines [9]. From that study it appeared that: (i) the best results in terms of conversion and selectivities are observed when using any phosphine having medium donating

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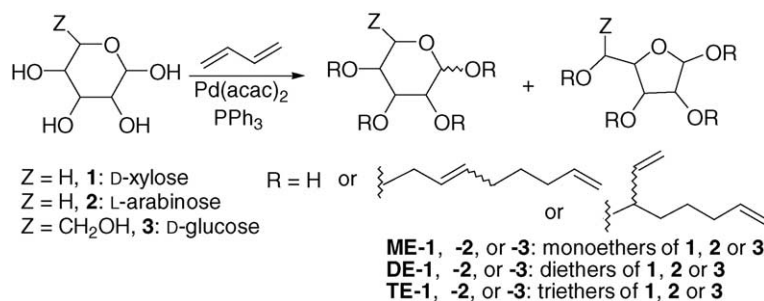
Scheme 1. Telomerization of butadiene with aldoses.

properties in DMF as the solvent, (ii) the monofunctionalization mainly occurs at the anomeric hydroxyl, affording the linear adduct as the major compound, (iii) the reaction efficiency does not greatly depend on the palladium precursor (Pd^0 or Pd^{II}).

Herein, we have furthered this study by a careful analysis of the butadiene/sugar concentration effects at room temperature and 75 °C. The concentration effect in the multiphase system employed is not simple, since for example, increasing the butadiene amount could, as expected, entail an increase of N [6,8,13,15], but could also have little or no influence [7,15]. Acceptable conditions for controlling the degree of etherification of some pentoses and hexoses have thus been found. Such a stepwise reaction has never been observed in non aqueous medium.

The hydrogenation of the resulting mono-octadienyl ethers (**ME**) and di-(octadienyl) ethers (**DE**) (Scheme 1) into saturated non-ionic surfactants has also been investigated, using the residual telomerization catalyst or a commercial palladium heterogeneous catalyst. Several commercial catalysts proved to be effective in these reactions and the telomerization catalyst also allowed the complete hydrogenation of the pentosides telomers; in contrast, one double bond remained in the glucosides octadienyl chains.

1. Results and discussion

We first determined the optimum reaction time required to synthesise monoethers (**ME-1**) of D-xylose using telomerization conditions close to those previously described [9]: 3 g of D-xylose with six equivalents of butadiene in the presence of 0.7 mol% $Pd(acac)_2$ and 1.4 mol% triphenylphosphine in 15 mL of DMF at 75 °C (entries 1–4, Table 1). The high conversion of D-xylose observed after 15 min (93%, entry 1) increased slightly in 25 min (97%, entry 2) and then remained constant (entries 3 and 4). Under these conditions, the reaction of monoethers (**ME-1**) with butadiene was sluggish, since the ratio (**ME-1/DE-1**) varied from 78/19 to 68/29 for a prolonged reaction time to 60 min. The influence of the relative butadiene amount was next studied. A two-fold quantity of butadiene afforded mono (**ME-1**) and di-octadienyl ethers (**DE-1**) in equal amounts (44% **ME-1** versus 48% **DE-1**,

entry 5). With a longer reaction time (2.5 h) and the use of 17 equivalents of butadiene, diether selectivity was increased to 60% (entry 6). As previously mentioned, sugar concentration also has a key role in product distribution [19]. Using the same relative amounts of butadiene/sugar as for entry 6 but with a three-fold decrease in D-xylose concentration, the monoethers (**ME-1**) were again the major products (63%), even when the catalyst and the reaction time were increased to 1.7 mol% and 3 h, respectively (entry 7). Thus, under these last conditions, the starting xylose was much more reactive in the telomerization reaction than the monoethers, although both concentrations decreased simultaneously. The lack of reactivity of **ME-1** can not only be explained by a concentration-kinetic effect, but also by the influence of the dissolved butadiene. Indeed, this is crucial to the reaction course as exemplified by the following general observation: at constant reactant amounts, an increase in solvent volume entails an increase of the butadiene dimers which, in turn, are detrimental to sugar transformation. Effectively controlling this parameter was difficult and turned out to be unnecessary at sugar concentration of 1.3 M or more. It is clear that the relative amount of butadiene and the sugar concentration are two crucial parameters which control mono- or diether formation.

At room temperature, the reaction proceeded much slower and a good selectivity could be easily achieved by changing the reaction time (entry 8). The reaction of D-xylose with 30 equivalents of butadiene in the presence of 2 mol% $Pd_2(dba)_3/2$ PPh_3 led to 95% conversion in 48 h, with a selectivity of 80% towards **ME-1**, while the diethers (**DE-1**) were the major products after 70 h (55%). Further increasing the reaction time led to a slight increase in **DE-1** selectivity, the yield of triethers (**TE-1**) being rather low even after 170 h of reaction.

In terms of conversion and degree of substitution, similar behaviour for xylose and arabinose was observed in the telomerization reaction, the differences appearing in the number of reactive forms [9] (pyranose for both sugars and furanose for arabinose). The telomerization of L-arabinose with six equivalents of butadiene in DMF (sugar, 1.3 M) at 75 °C for 15 min led to 67% of the monoethers (**ME-2**) (entry 9) and this value remained unchanged for a reaction time prolonged to 1 h (entry 10). In the presence of 17 equivalents of

Table 1
Palladium catalyzed telomerization of butadiene with aldoses **1**, **2**, **3**[a]

Entry	Aldose, solvent (mmol/mL)	C_4H_8			Conversion[c] (%)	Selectivity[c] (%) **ME/DE/TE** (isolated (%))[d]	N[e]
		Pd[b]	Equivalent	Time			
1	**1**, DMF (20/15)	A	6	15 min	93	78[f]/19/3 (**ME-1** (54))	1.3
2	**1**, DMF (20/15)	A	6	25 min	97	74[f]/23/3 (**ME-1** (54))	1.3
3	**1**, DMF (20/15)	A	6	35 min	97	69[f]/28/3 (**ME-1** (54))	1.3
4	**1**, DMF (20/15)	A	6	1 h	97	68[f]/29/3 (**ME-1** (54))	1.3
5	**1**, DMF (20/15)	A	12	1 h	98	44[f]/48/8 (**ME-2** (55))	1.6
6	**1**, DMF (20/15)	A	17	2.5 h	100	24[f]/60/16 (**ME-2** (55))	1.9
7	**1**, DMF (3.3/7.5)	B	17	3 h	84	63[f]/33/4 (**ME-2** (55))	1.4
8	**1**, DMF (1.8/4)	C	30	32 h	76	88[f]/12/0 (**ME-2** (55))	1.1
				48 h	95	80/20/0 (**ME-2** (55))	1.2
				70 h	99	33/55/12 (**ME-2** (55))	1.8
				170 h	100	18/59/23 (**ME-2** (55))	2.0
9	**2**, DMF (20/15)	A	6	15 min	98	67/31/2 **ME-2** (55)	1.4
10	**2**, DMF (20/15)	A	6	1 h	96	68/31/1 (**DE-2** (52))	1.3
11	**2**, DMF (20/15)	A	17	2.5 h	100	37/52/11 (**DE-2** (52))	1.7
12	**3**, DMF (20/15)	A	6	15 min	97	62/35/3 (**ME-1** (55%))	1.4
13	**3**, DMF (20/15)	A	17	2.5 h	100	25/53/22 (**ME-1** (55%))	2.0
14	**1**, DMAE (20/15)	A	6	25 min	90	74[g]/24/2 (**ME-1** (55%))	1.2
15	**1**, DMAE (20/15)	D	6	4 h	100	75/23/2 **ME-1** (10%)	1.2

[a] Reactions conditions: autoclave of 50 mL, 75 °C (except with system C, 20 °C).

[b] Catalytic system: A, 0.7 mol% of Pd(acac)$_2$, 1.44 mol% of PPh$_3$; B, 1.7 mol% of Pd(acac)$_2$, 3.4 mol% of PPh$_3$; C, 2 mol% of Pd$_2$(dba)$_3$ CHCl$_3$, 4 mol% of PPh$_3$; D, 0.05 mol% of Pd(acac)$_2$, 0.1 mol% of PPh$_3$.

[c] GC evaluation.

[d] Isolated compound (yield).

[e] N = average degree of substitution = average number of octadienyl chains per aldose unit.

[f] α/β-anomer ratio (sum of linear + branched isomers) is 30/70.

[g] α/β-anomer ratio (sum of linear + branched isomers) is 25/75.

butadiene, **DE-2** became the major compound (52%, entry 11). In both cases, the selectivities for **ME-2** and **DE-2** were slightly lower than with D-xylose (entries 9 and 11 versus 1 and 6).

Next, we tested D-glucose as a substrate possessing a primary hydroxyl group which could be more reactive than a secondary one in the telomerization reaction [16,20]. Acceptable selectivities for **ME-3** and **DE-3** were again achieved in the presence of 6 and 17 equivalents of butadiene, respectively (entries 12 and 13).

The telomerisation reaction selectivities were similar with L-arabinose and D-glucose and slightly better with D-xylose. Thus, whatever the starting carbohydrate telogen, the above conditions were convenient for the monoether and diether synthesis, reproducible results being easily obtained.

To test the influence of a protic solvent on telomerization control, we carried out the reaction of D-xylose with butadiene in *N,N*-dimethylaminoethanol (DMAE) which is known to be inert as a telogen [21]. In this protic polar solvent, the rate and the selectivity for the monoethers were similar to those observed in DMF (entry 14). DMAE being a more volatile solvent than DMF, its use is advantageous due to easier elimination. However, when the catalyst loading was decreased to 0.05 mol%, resulting in an increase of the reaction time up to 4 h for full sugar conversion, only 10% of **ME-1** was isolated (entry 15). In a separate experiment, we have observed a slow evolution of D-xylose in refluxing DMAE under an inert atmosphere, even in the absence of a metal catalyst. It seems that the dimethylamino group is basic enough to induce aldose isomerisation or decomposition [22]. In each entry of Table 1 (except entry 15), isolated yields of **ME** or **DE** were 52–55%. Thus, DMAE could be preferred for the preparation of monoethers and DMF remains the solvent of choice for the synthesis of the diethers which requires prolonged heating times.

Next, we undertook the identification of the telomers, those of **ME-1, 2** having been previously characterised [9,19]. The GC–MS analysis of peracetylated samples of the crude reaction revealed the presence of complicated mixtures of **ME-1-3** and **DE-1-3**. The **ME** and **DE** groups of the unprotected ethers were easily separated by chromatography or, after peracetylation, by chromatography or vacuum distillation. The partial separation of the peracetylated monoethers was carried out by flash chromatography and their structures compared to authentic samples obtained via the telomerization of partially *O*-protected aldoses [19]. Fig. 1 summarises these structures and Table 2 shows the isomeric composition of the **ME-1-3** fractions, thus allowing a comparison of pentose and glucose behaviour.

When D-xylose reacted with butadiene in DMF, regio- and stereoisomers of octadienyl xylopyranosides constituted more than 95% of the **ME-1** (Table 2, entry 1). The α- and β-anomers of the 2,7-octadien-1-yl xylopyranosides (**4l**, linear isomers) were the major products (81%) (Fig. 1) and each of them showed a typical *E/Z*-distribution of about 8:1. The α- and β-anomers of 1,7-octadien-3-yl xylopyranosides (**4b**,
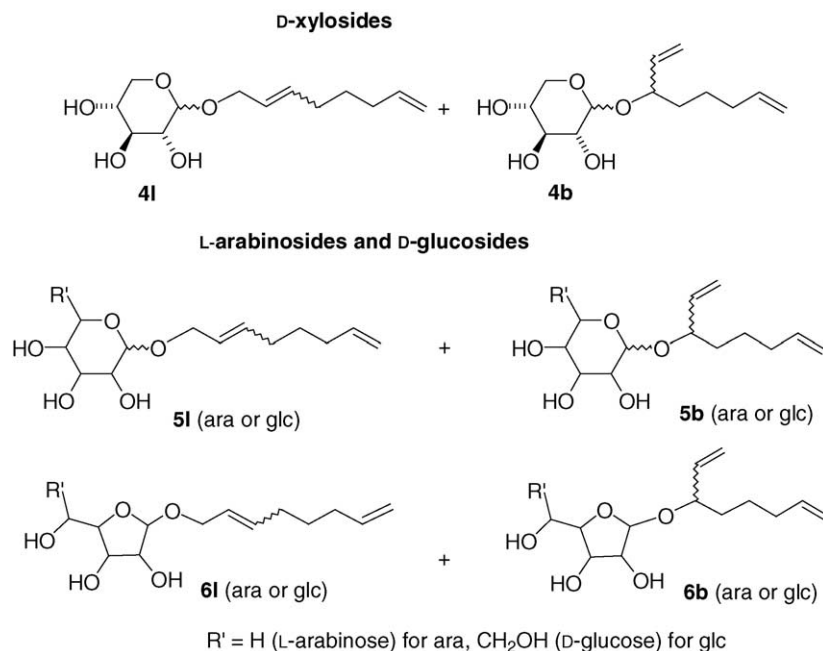
Fig. 1. Structures of the identified monoethers (**ME**).

Table 2
Repartition of monoethers resulting of the telomerization of butadiene with aldoses

Entry (conditions)[a]	Aldose	Pyranosides[b], Products l%, b%	Furanosides[b] Products l%, b%	Ratios l/b[c]; α/β[d]	Other **ME**[e]
1 (Entry 1)	**1**	**4l/4b**, 81, 14	0	85:15, 30:70	5
2 (Entry 7)	**1**	**4l/4b**, 90, 5	0	95:5, 30:70	5
3 (Entry 9)	**2**	**5l/5b** (ara), 29, 7	**6l/6b** (ara), 48, 10	82:18, 25:75	6
4 (Entry 11)	**2**	**5l/5b** (ara), 29, 8	**6l/6b** (ara), 48, 10	80/20	6
5 (Entry 12)	**3**	**5l/5b** (glc), 70, 12	**6l/6b** (glc), 12, 0	87/13	5
6 (Entry 13)	**3**	**5l/5b** (glc), 71, 12	**6l/6b** (glc), 12, 0	87/13	4
7 (Entry 14)	**1**	**4l/4b**, 68, 12	nd[f]	nd[f]	20[g]

[a] Reactions conditions correspond to those described in Table 1.
[b] GC evaluation.
[c] Total ratio of l/b isomers.
[d] α/β-anomer ratio (sum of linear + branched isomers).
[e] Two or more compounds which structures were not determined.
[f] Not determined.
[g] The flash chromatography of the complicated reaction mixture allowed to detect more than four additional products with closed retention times (GC/mass). They were tentatively identified as α/β-octa-2,7-dien-1-yl xylofuranosides on the basis of their mass spectra exhibiting molecular ion (CI: $M + NH_4^+ = 402$) and characteristic fragments (259, 217, 141).

branched isomers; each of them corresponding to a mixture of two epimers) were also formed in a significant amount (14%).

The composition of the monoethers **ME-2** and **ME-3** obtained from L-arabinose and D-glucose was more complicated (Fig. 1, Table 2, entries 3–6). The major products again arose from the reaction of butadiene with the anomeric hydroxyl of L-arabinose and D-glucose. However, in addition to the linear and branched α/β-pyranosides **5**, the linear and branched isomers of α/β-furanosides **6** were also formed. The furanosides were even the major products (58%) in the case of L-arabinose.[1]

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[1] Contrarily to our previous assertion [9] and as verified by GC of authentic samples, the major octadienylarabinosides consist of furanosides instead of pyranosides.

The α/β-anomer composition of the monoethers obtained from D-xylose (ratio of total amounts of linear and branched xylopyranosides isomers) was almost constant in all experiments carried out in DMF (70/30, entries 1–8, Table 1). In DMAE as the solvent, the **4α/4β**-xylopyranoside ratio increased to 75/25 and a few additional isomers of octadienyl ethers were observed (Table 2, entry 2). On the other hand, the ratio of linear/branched (**l/b**) regio-isomers (**4l/4b**) depended on the relative amounts of introduced reactants (Table 2, entries 1, 2). The **l/b** variations were less important with L-arabinose or D-glucose (Table 2, entries 3–6, respectively).

As previously observed for the monoether composition, certain characteristic features were again found [9,19]. The distribution of pyranosides/furanosides as well as
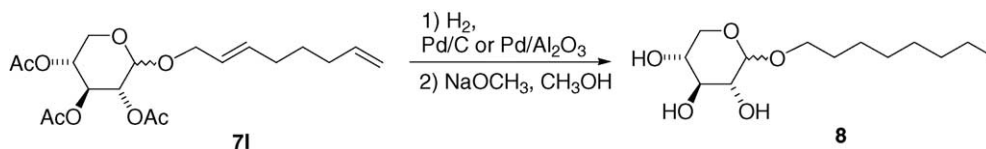
Scheme 2. Access to saturated xylopyranosides.

α/β-anomers is related to the tautomeric forms of the starting sugar. The telomerization of butadiene with carbohydrates proceeds under kinetic control [19] as in the case of simple alcohols [23] and the ratio of telomers does not depend on the starting composition but on the relative rates of tautomer transformation. This could explain the changes observed in the isomer distribution with experimental conditions (Table 2). Another point to emphasise in monoether production is the good chemoselectivity towards the etherification of the anomeric hydroxyl under all conditions employed [9] and whatever the starting sugar, with or without a primary hydroxy group (Fig. 1). In contrast, and as indicated by GC–MS, the formation of diethers (**DE**) was not chemoselective, the different hydroxyls of glycosides **5** and **6** reacting similarly with butadiene. Reaction of a primary hydroxyl was not faster than a secondary one, as observed when comparing the monoethers obtained in the telomerization of L-arabinose in the presence of 6 and 17 equivalents of butadiene (Table 2, entries 3, 4). The relative ratio of octadienyl furanosides (**6**) and octadienyl pyranosides (**5**) did not change when a higher degree of substitution was achieved. This indicated that the furanosides (**6** ara) having a primary hydroxyl group exhibited the same reactivity as the pyranosides (**5** ara) which only have secondary hydroxyls. The greater reactivity of the anomeric hydroxyl could, as previously noted [9], be attributed to its higher acidity than that of other hydroxyl groups [24]. The second etherification seems to occur statistically and much slower, allowing a good selectivity for the monoethers. The introduction of the third octadienyl chain proceeds still more slowly probably due to an enhanced steric hindrance.

Our further studies dealt with the hydrogenation of the monoethers in order to prepare the more stable saturated surfactants [17]. This reaction, which can be complicated by a cleavage reaction [15,17], was first examined with the peracetylated xylopyranosides **7l** (Scheme 2). With cyclohexane as solvent and 5% Pd/Al$_2$O$_3$ catalyst under 10 atm. of hydrogen at 70 °C, the saturated compounds were obtained quantitatively and without side reaction. The hydrogenation experiments were also successful when using a 10% Pd/C catalyst in methanol under 1 atm. of hydrogen, starting from the above peracetylated xylosides or from the crude mixture of O-acetyl protected monoethers **ME-1**. The deacetylation was performed with sodium methoxide in methanol, leading to saturated glycosides **8** (or saturated **ME-1**) in 94–97% overall yield.

In the aim of simplifying access to the saturated compounds, the residual telomerization catalyst was used to promote the subsequent hydrogenation reaction. Thus, the mixture resulting from the butadiene telomerization with L-arabinose (Table 1, entry 9) was evaporated under vacuum, dissolved in methanol and stirred for one day under an hydrogen atmosphere. The expected saturated monoethers were obtained in 55% isolated yield by flash chromatography.

In the case of D-glucose, however, one double bond remained after hydrogenation under these latter conditions leading to octenyl mono- and diethers (Scheme 3). The hydrogenation of the octenyl chain of a monoether **ME-9** using a more active 10% Pd/C catalyst was also unsuccessful in methanol because **9** and **10** precipitate, preventing their further hydrogenation. The use of ethanol for hydrogenation was successful as the octyl ethers were soluble in this solvent. Unfortunately, the residual telomerization catalyst was not effective for the complete hydrogenation of the octadienyl chain of a mixture of **5** (glc) and **6** (glc) using EtOH as the solvent, since once again **9** and **10** were identified, even under 20 atm. of hydrogen pressure. Thus, a general way to glucose saturated monoether derivatives requires the separation of their octadienyl telomer precursors, followed by hydrogenation using a Pd/C catalyst system in EtOH.
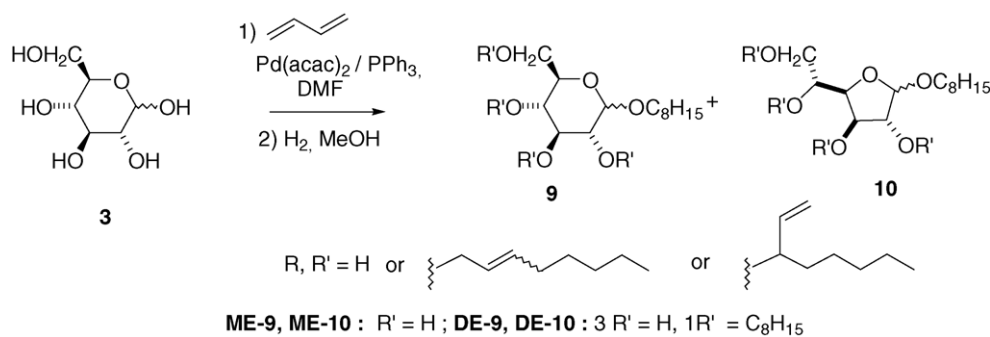
Scheme 3. Hydrogenation of the glucose ethers.

In conclusion, the controlled etherification of aldoses by one or two octadienyl chains using the Pd-catalysed telomerization of butadiene, is possible in organic solvents. Only minor changes of the reaction conditions are necessary to control the grafting by either modifying the reaction time at room temperature or the butadiene relative amount at 75 °C for a sugar concentration ≥1.3 M. The groups of mono- and diethers are separable by fractional distillation or flash chromatography after peracetylation of the crude mixture and the double bonds can be hydrogenated. Thus, the telomerization reaction and the hydrogenation of the resulting telomers open a straightforward way from aldoses to non-ionic surfactants with different properties.

2. Experimental

The general procedure for the telomerization and product analysis have been described in our previous articles [9,19]. 5% Pd/Al$_2$O$_3$ was purchased from Acros Chemical and 10% Pd/C was a gift from Johnson-Matthey. Solvents were distilled under argon after drying over CaH$_2$ (DMF), sodium (MeOH) or molecular sieves (*N,N*-dimethylaminoethanol). All distilled solvents were stored over molecular sieves (4 Å) under an inert atmosphere. 1,3-Butadiene was flash distilled prior to use.

2.1. Analysis and products characterisation

The conversion and the ratio of isomeric products (Table 1) were determined by GC. To obtain an adequate GC response, the acetylation of reaction samples (0.1 mL) by acetic anhydride (0.2 mL) in the presence of pyridine (0.05 mL) was performed. The separation of the mono- and diethers was achieved by flash chromatography (CH$_2$Cl$_2$/MeOH: 98/2 to 90/10) or (petroleum ether/AcOEt: 70/30) for the unprotected sugars or for the corresponding peracetylated compounds, respectively.

2.1.1. D-Xylose monoethers

For the telomerization carried out in DMF, the GC–MS analysis of the acetylated reaction mixture revealed the presence of ten monoether isomers of with $[M+18]^+ = 402[MS(CI)]$. The monoethers were partially separated by flash chromatography of the acetylated reaction mixture. The peracetylated monoethers could also be extracted from the mixture by distillation under vacuum (10^{-3} Torr). The retention times of the major compounds and their NMR and mass spectra were identical to those of authentic samples of triacetylated **4l** (α and β compounds having *Z*- or *E*-configuration of the double bond) and **4b** derivatives [9,19] (α and β compounds). Two minor signals (about 5%) were not identified. For the telomerization reaction in *N,N*-dimethylaminoethanol, the newly formed isomers were not fully characterised since authentic samples were not available (Table 2, entry 2). The results are summarised in Table 2, entries 1, 2 and 7.

2.1.2. L-Arabinose monoethers

GC–MS analysis of the peracetylated reaction mixture revealed the presence of fourteen isomers of monoethers **5** and **6** (ara) with close retention times and $[M+18]^+ = 402[MS(CI)]$. The monoethers were partially separated by flash chromatography of the acetylated reaction mixture. The retention times of the major compounds and their NMR and mass spectra were identical to those of authentic samples of triacetylated **5l** (ara) (α and β- compounds having *Z*- or *E*-configuration of the double bond) and **5b** (ara) derivatives [19] (α and β compounds). For the furanose forms, acetylated α- and β-**6l** having the *E*-configuration of the double bond has been previously described [9]. To confirm the structures of the branched isomers **6b**, we compared the corresponding saturated compounds with those arising from the following sequence: telomerization of 2,3,5-tri-*O*-benzyl-β-D-arabinofuranose with butadiene followed by the hydrogenation/deprotection reaction. Two minor signals (about 6%) were not identified. The results are summarised in Table 2, entries 3, 4.

2.1.3. D-Glucose monoethers

GC–MS analysis of the acetylated reaction mixture revealed the presence of nine isomers of monoethers **5**, **6** (glc) with $[M+18]^+ = 474[MS(CI)]$. Their structures were determined after their partial hydrogenation (see later) or their complete hydrogenation.

2.1.4. Hydrogenation over Pd/Al$_2$O$_3$

Octa-2′,7′-dien-1′-yl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (**11β**) (755 mg, 1.97 mmol) was dissolved in cyclohexane (5 mL) and transferred into a 50 mL stainless steel autoclave, which had been charged with 5% Pd/Al$_2$O$_3$ (302 mg) under Ar. The autoclave was pressurised with hydrogen to 10 bar and heated at 70 °C. After stirring the mixture for 8 h, unconsumed hydrogen was vented, the solvent evaporated and 1′-octyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside was separated by flash chromatography (petroleum ether/AcOEt 70:30). Yield: 742 mg (97%). ^{1}H NMR (CDCl$_3$): 0.77 (t, $J = 5.6$ Hz, 3H, H8′), 1.14 (m, 10H, H3′, H4′, H5′, H6′, H7′), 1.43 (m, 2H, H2′), 1.92 (s, 3H, Ac), 1.94 (s, 6H, Ac), 3.25 (dd, $J = 11.9, 9.1$ Hz, 1H, H5), 3.35 (dt, $J = 9.6, 6.3$ Hz, 1H, H1′), 3.70 (dt, $J = 9.6, 6.3$ Hz, 1H, H1′), 4.01 (dd, $J = 11.7, 5.0$ Hz, 1H, H5), 4.37 (d, $J = 6.8$ Hz, 1H, H1), 4.79 (dd, $J = 8.5, 6.8$ Hz, 1H, H2), 4.80–4.85 (m, 1H, H4), 5.06 (t, $J = 8.5$ Hz, 1H, H3). ^{13}C NMR (CDCl$_3$): 13.81 (C8′), 20.98, 21.00, 21.31 (3C, CH$_3$CO), 22.96, 25.61, 28.99 (2C), 29.17, 31.53 (C2′, C3′, C4′, C5′, C6′, C7′), 61.72 (C5), 68.66 (C4), 69.42 (C1′), 70.59 (C2), 71.39 (C3), 100.41 (C1), 169.06, 169.52, 169.78 (3CH$_3$CO). MS(CI) *m/z* 406 (100, $M+18^+$), 348 (5), 259 (69), 201 (11), 199 (10), 158 (10), 141 (46), 128 (22), 114 (19), 77 (85). Anal. Calcd. for C$_{19}$H$_{32}$O$_8$ (388.5): C, 58.75; H, 8.30. Found: C, 58.54; H, 8.58.

2.1.5. Hydrogenation over Pd/C

To a solution of octa-2′,7′-dien-1′-yl 2,3,4-tri-*O*-acetyl-α-D-xylopyranoside (**4l**) (436 mg, 1.14 mmol) in MeOH (20 mL), was added 10% Pd/C (43 mg). The reaction mixture was stirred under 1 atm. of hydrogen pressure for 12 h at room temperature. The reaction mixture was filtered through Celite and evaporated under reduced pressure to give 430 mg (98%) of 1′-octyl 2,3,4-tri-*O*-acetyl-α-D-xylopyranoside. ^{1}H NMR (CDCl$_3$): 0.81 (t, *J* = 5.6 Hz, 3H, H8′), 1.18 (m, 10H, H3′, H4′, H5′, H6′, H7′), 1.45 (m, 2H, H2′), 1.96 (s, 6H, Ac), 1.98 (s, 3H, Ac), 3.31 (dt, *J* = 9.7, 6.5 Hz, 1H, H1′), 3.57 (d, *J* = 11.0 Hz, 1H, H5), 3.61 (dt, *J* = 9.7, 6.5 Hz, 1H, H1′), 3.69 (dd, *J* = 11.0, 6.1 Hz, 1H, H5), 4.72 (dd, *J* = 10.3, 3.6 Hz, 1H, H2), 4.86 (dd, *J* = 10.0, 6.1 Hz, 1H, H4), 4.92 (d, *J* = 3.6 Hz, 1H, H1), 5.41 (t, *J* = 9.6 Hz, 1H, H3). ^{13}C NMR (CDCl$_3$): 14.38 (C8′), 20.94, 20.98, 21.03 (3C, CH$_3$CO), 22.94, 26.34, 29.60 (2C), 29.56, 32.12 (C2′, C3′, C4′, C5′, C6′, C7′), 58.50 (C5), 68.75 (C1′), 69.90 (C4), 70.01 (C3), 71.47 (C2), 95.92 (C1), 170.21, 170.31, 170.47 (3CH$_3$CO). MS(CI) *m/z* 406 (100, *M* + 18$^+$), 348 (2), 259 (39), 201 (5), 199 (7), 141 (20), 127 (18), 114 (11), 77 (60).

The mixture of *O*-acetyl protected monoethers **ME-1** (8 isomers) (136 mg, 0.35 mmol) was hydrogenated under the same conditions giving 131 mg (96%) of the saturated compounds (6 isomers). No signal of a double bond was observed in ^{1}H and ^{13}C NMR spectra of the hydrogenated sample.

2.1.6. Hydrogenation of telomers using the telomerization catalyst

The reaction mixture obtained from the telomerization reaction was evaporated at 50 °C under reduced pressure. The residue was dissolved in CH$_3$OH (20 mL) and transferred into a 50 mL stainless steel autoclave. The autoclave was pressurised with hydrogen to 17 bar and heated to 50 °C. After stirring for 24 h, unconsumed hydrogen was vented and the solvent evaporated. The products were partially separated by flash chromatography (CH$_2$Cl$_2$/CH$_3$OH 100:0 to 95:5 and 90:10). The following major isomers have been identified.

2.1.7. 2′-(E)-octen-1′-yl β-D-glucopyranoside (9β-l)

^{1}H NMR (CDCl$_3$): 0.84 (t, *J* = 6.8 Hz, 3H, H3′), 1.26–1.45 (m, 6H, H4′,6′), 1.99–2.13 (m, 2H), 3.19–3.33 (m, 2H), 3.36–3.48 (m, 2H), 3.72 (dd, *J* = 11.8, 4.8 Hz, 1H), 3.89 (d, *J* = 11.1 Hz, 1H), 4.12 (dd, *J* = 11.8, 6.5 Hz, 1H), 4.34 (m, 2H), 4.81 (s, 4H), 5.61 (dt, *J* = 15.4, 6.7 Hz, 1H, H3′), 5.71 (dt, *J* = 15.4, 6.7 Hz, 1H, H3′). ^{13}C NMR (CD$_3$OD): 15.50 (C8′), 24.49 (C7′), 31.31, 33.44, 34.22 (C4′, C5′, C6′), 63.55 (C6), 71.80 (C1′), 72.29 (C4), 75.73 (C2), 78.58 (C5), 78.80 (C3), 103.71 (C1), 128.05 (C3′), 136.94 (C2′).

2.1.8. 2′-(E)-octen-1′-yl α-D-glucopyranoside (9α-l)

^{13}C NMR (CD$_3$OD): 15.38 (C8′), 24.52 (C7′), 31.18, 33.33, 34.11 (C4′, C5′, C6′), 63.43 (C6), 69.89 (C1′), 72.32 (C4), 74.08 (C5), 74.31 (C2), 75.80 (C3), 99.53 (C1), 127.94 (C3′), 136.74 (C2′).

2.1.9. 2′-(E)-octen-1′-yl α-D-glucofuranoside (10β-l)

^{13}C NMR (CD$_3$OD + CDCl$_3$): 14.97 (C8′), 24.04 (C7′), 30.38, 32.99, 33.78 (C4′, C5′, C6′), 65.75 (C6), 69.85 (C1′), 73.62 (C5), 77.72 (C3), 82.70 (C2), 83.21 (C4), 109.03 (C1), 127.56 (C3′), 136.55 (C2′).

2.1.10. 2′-(E)-octen-1′-yl α-D-glucofuranoside (10α-l)

^{13}C NMR (CD$_3$OD + CDCl$_3$): 14.97 (C8′), 24.04 (C7′), 30.38, 32.99, 33.78 (C4′, C5′, C6′), 65.30 (C6), 70.49 (C1′), 72.44 (C5), 78.12 (C3), 79.51 (C2), 79.66 (C4), 102.36 (C1), 127.56 (C3′), 136.55 (C2′).

2.1.11. 2′-octen-3′-yl β-D-glucofuranoside (12α-b)

^{13}C NMR (CD$_3$OD + CDCl$_3$): major epimer: 14.99 (C8′), 24.44 (C7′), 26.44, 33.78, 36.88 (C4′, C5′, C6′), 63.28 (C6), 72.15 (C4), 75.67 (C2), 78.19 (C5), 78.56 (C3), 83.33(C3′), 103.58 (C1), 116.59 (C1′), 141.45 (C2′). Minor epimer: 14.99 (C8′), 24.04 (C7′), 26.09, 33.48, 36.05 (C4′, C5′, C6′), 63.15 (C6), 71.95 (C4), 75.41 (C2), 78.13 (C5), 78.56 (C3), 80.23 (C3′), 101.02 (C1), 119.12 (C1′), 140.05 (C2′).

The reaction mixture obtained with D-glucose telomerization (Table 1, entry 12) was hydrogenated using EtOH as the solvent instead of methanol as described above. The monoethers were obtained in 57% yield by flash chromatography. Their ^{1}H and ^{13}C NMR data revealed the presence of internal double bonds (δ_C, 120–130) in significant amounts. The full characterisation of this complex mixture was not attempted.

The **10β-l** isomer was hydrogenated using the 10% Pd/C catalyst in EtOH: 1′-oct-yl β-D-glucopyranoside: 97%. ^{1}H NMR (CD$_3$OD): 0.80 (br. t, *J* = 6.8 Hz, 3H, H8′), 1.15–1.45 (m, 10H, H3′,4′,5′,6′,7′), 1.46–1.61 (m, 2H, H2′), 3.01–3.12 (m, 1H), 3.13–3.35 (m, 3H), 3.37–3.50 (m, 1H), 3.52–3.69 (m, 1H), 3.72–3.88 (m, 1H), 3.95–3.99 (m, 1H), 4.17 (d, *J* = 7.9 Hz, 1H, H1), 4.92 (br. s, 4H, OH). ^{13}C NMR (CDCl$_3$): 14.96 (C8′), 24.18 (C7′), 27.56, 30.88, 31.05, 31.23 33.46 (C2′, C3′, C4′, C5′, C6′), 63.16 (C6), 71.33 (C1′), 72.01 (C4), 75.48 (C2), 78.25 (C5), 78.47 (C3), 104.73 (C1).

2.2. Deprotection of some acetylated octyl xylosides

2.2.1. 1′-Octyl α-D-xylopyranoside (8α)

Oct-1′-yl 2,3,4-tri-*O*-acetyl-α-D-xylopyranoside (450 mg, 1.16 mmol) was dissolved in anhydrous MeOH (6 mL). Sodium (150 mg, 6.50 mmol) was added and the solution stirred for 12 h at room temperature. The reaction mixture was treated with water (1 mL) and concentrated under vacuum. The residue was taken up in a mixture of ethyl acetate (10 mL) and water (5 mL). The organic layer was separated, washed with water, dried over anhydrous MgSO$_4$ and evaporated to give 282 mg (93%) of the product. ^{1}H NMR (CD$_3$OD): 0.92 (t, *J* = 6.5 Hz, 3H, H8′), 1.34 (m, 10H, H3′, H4′, H5′, H6′ H7′), 1.54 (m, 2H, H2′), 3.35 (m, 7H), 4.60 (d, *J* = 7.5 Hz, 1H, H1), 4.78 (br. s, 3H, OH). ^{13}C NMR (CD$_3$OD): 15.27 (C8′), 24.53, 28.05, 31.23, 31.39, 31.45, 33.83 (C2′, C3′, C4′, C5′, C6′ C7′), 63.71 (C5), 70.04 (C1′), 72.34 (C4), 74.43

(C3), 76.02 (C2), 101.13 (C1). Anal. Calcd. for $C_{13}H_{26}O_5$ (262.3): C, 59.52; H, 9.99. Found: C, 59.24; H, 10.00.

1′-Octyl β-D-xylopyranoside (**8β**) was obtained in 97% yield (426 mg) from 650 mg (1.67 mmol) of oct-1′-yl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside using the same procedure described above. ^{1}H NMR (CD$_3$OD): 0.92 (t, $J = 6.2$ Hz, 3H, H8′), 1.32 (m, 10H, H3′, H4′, H5′, H6′, H7′), 1.61 (m, 2H, H2′), 3.19 (dd, $J = 8.5, 7.5$ Hz, 1H, H2), 3.20 (t, $J = 10.5$ Hz, 1H, H5), 3.32 (t, $J = 9$ Hz, 1H, H3). 3.47–3.52 (m, 1H, H4), 3.54 (dt, $J = 18.0, 7.5$ Hz, 1H, H1′), 3.83 (dt, $J = 18.0, 7.5$ Hz, 1H, H1′), 3.87 (dd, $J = 10.5, 5.2$ Hz, 1H, H5), 4.21 (d, $J = 7.5$ Hz, 1H, H1). ^{13}C NMR (CD$_3$OD): 15.37 (C8′), 24.47, 27.84, 31.17, 31.30, 31.54, 33.75 (C2′, C3′, C4′, C5′, C6′, C7′), 67.50 (C5), 71.80 (C1′), 71.91 (C4), 75.53 (C2), 78.54 (C3), 105.63 (C1).

Acknowledgments

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