Palladium-Catalyzed Telomerization of Butadiene with Tri-*O*-acetylated Pentoses as a Convenient Route to 2,7-Octadienyl Glycosides

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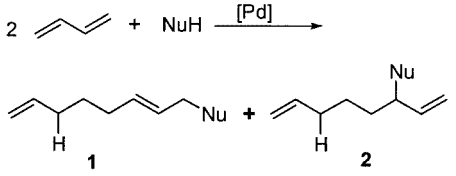
Palladium-catalyzed telomerization of butadiene with *O*-acetylated pyranoses having a free anomeric hydroxyl group was applied for synthesis of octadienyl glycosides. The ratio of linear to branched glycosides depends dramatically on the conditions used. By careful optimization of reaction parameters the highly selective formation (95:5) of linear glycosides was achieved. An extended mechanism of the telomerization reaction is proposed.

Introduction

The palladium-catalyzed telomerization of butadiene with phenol, which is one of the oldest palladium-catalyzed transformations in organic chemistry, was reported as early as 1967[1] (Scheme 1, Nu = PhO).



Scheme 1

The synthesis of functionalized octadienes starting from cheap compounds in a 100% atom-efficient manner[2–4] is very attractive. Since the first report, the telomerization of butadiene with different nucleophiles, such as alcohols, amines, acids, and active methylene compounds, has attracted keen and constant interest.[5–7] Indeed the telomerization reaction has proven to be of considerable industrial value.[8–12] Depending on the nucleophile used, the products obtained could play an important role as surfactants,[11–15] plasticizers,[16,17] and components of diesel fuels,[18,19] or as intermediate chemicals in the production of fine chemicals and natural products.[20,21] However, although many patents have appeared, the synthesis of 2,7-octadien-1-ol starting from butadiene and water seems to be the only industrial application of the telomerization reaction realized so far.[22–24] This reflects clearly the difficulties that are encountered in catalyst loading and recycling as well as in the regioselectivity of the nucleophilic addition. The 1,6- and 3,6-addition of the telogen in the course of the catalytic reaction leads to two regioisomers (**1** and **2**) which are difficult to separate. The regioselectivity of the telomerization reaction is strongly dependent on the nucleophile.[5–7] Water and monofunctional alcohols give linear isomers (**1**) in high yields while significant amounts of branched isomers (**2**) can be detected when phenols or carboxylic acids are used as nucleophiles.

Among these reactions, the telomerization of butadiene with sugars attracts considerable industrial interest as a simple route to non-ionic surfactants.[25–30] Carbohydrates react as polyfunctional nucleophiles, leading to a complex mixture of mono-, di-, and polyethers. The telomerization of butadiene with *O*-protected sugars is limited to a single example where a primary hydroxyl group of protected galactopyranose was used as a nucleophile.[30] To the best of our knowledge, *O*-protected sugars with a free anomeric hydroxyl group have never played the role of the nucleophilic partner in the telomerization, although the non-selective telomerization of unprotected carbohydrates[14] clearly demonstrates the possibility for this reaction to occur. Such telomerization would lead to precursors of *n*-octyl glycosides which, besides their use as non-ionic surfactants,[26–31] are of considerable interest as intermediates in the synthesis of enantiopure ligands,[32] as models in enzymatic processes,[33] and in artificial receptor chemistry.[34]

Herein we report the results of a detailed survey of reaction parameters in the palladium-catalyzed telomerization of butadiene with *O*-acetylated pentopyranoses having an anomeric hydroxyl group, and conditions for the selective production of the linear isomer.

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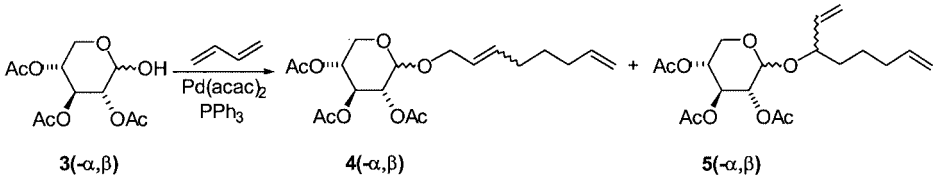
Results and Discussion

As a starting point of our investigation, we tested the telomerization of butadiene with 2,3,4-tri-*O*-acetyl-D-xylopyranose (**3**) in the presence of $Pd(acac)_2$ and triphenylphosphane in DMF at 75 °C in a 50-mL stainless steel autoclave reactor (Scheme 2, Table 1).

The *O*-protected sugar (**3**) was sluggish towards the telomerization reaction. When compound **3** was reacted for 1.5 h at 75 °C in DMF, with a tenfold excess of butadiene in the presence of 2 mol% $Pd(acac)_2$ and 4 mol% PPh_3, only 31% of telomers were obtained (Table 1, entry 1). A nearly quantitative yield of telomers was observed in the presence of a large excess of butadiene (45 equivalents) (entry 2). Surprisingly, the reaction efficiency was directly related to the substrate loading. For example, tripling the amounts of reagents and solvent led to an increase in the telomer yield (from 31 to 58%, entries 1 and 3). Since the reaction is carried out in an autoclave of constant volume (50 mL), the butadiene concentration in solution is dependent on the gas−liquid equilibrium; modification of the gas/liquid phase ratio causes significant changes of this equilibrium and therefore of the reaction rate. The catalyst loading is also an important factor: when the quantities of $Pd(acac)_2$ and PPh_3 were respectively decreased to 1 and 2 mol%, conversion of the starting xylopyranose derivative did not exceed 8%, even if the reaction was prolonged to 7 h (entry 4).

A GC/MS study of the reaction products revealed the formation of complicated mixtures of isomeric telomers and oligomeric by-products including 1,3,7-octadiene, 4-vinylcyclohexene, and isomeric tri- and tetramers of butadiene. Separation by flash chromatography allowed isolation of the telomer adducts, whose structures, established by ^1H and ^{13}C NMR spectroscopy, proved to be linear 2,7-octadienyl- and branched 1,7-octadien-3-ylxylopyranosides [(**4α**, **4β**) and (**5α**, **5β**)]. The linear glycosides **4α** and **4β** were the major products and showed a typical *Z*-/*E*- distribution about 1:8 whatever the experimental conditions used. Each of the branched xylopyranosides **5α** and **5β** was obtained as a mixture of two diastereomers with a different configuration at the C-3 stereocenter. The overall ratio of α/β-anomers [(**4α** + **5α**)/(**4β** + **5β**)] was similar in all experiments, close to 1:1 and different from that in the starting xylopyranose **3** which is about 2:1. It has been shown that, in pure solvents such as acetonitrile or chloroform without any trace of impurities or protic sources, the α/β anomer ratio of **3** remains constant.[35] On the contrary, under catalysis, mutarotation takes place with rates depending on the type of catalysis, as we observed in our NMR analysis (see Expt. Sect., Table 5): the **α/β** equilibrium about 2:1 was attained in about 36 h in $CDCl_3$ and 12 h in CD_3CN containing traces of water, while less than an hour was required in CD_3CN/HCl. Obviously, we were not able to evaluate the real position of the equilibrium in our telomerization medium, but we could reasonably assume an **α/β** ratio > 1 since the α-isomer was largely predominant whatever the catalysis conditions, as exemplified in Table 5. The loss of the stereochemistry of the starting xylopyranose could thus be due to a rapid catalyzed mutarotation compared to the rate of the telomerization reaction (Scheme 3). The **3β**-anomer with an *equatorial* hydroxyl in the preferential conformation would be more reactive in the telomerization with butadiene; this will be discussed later.

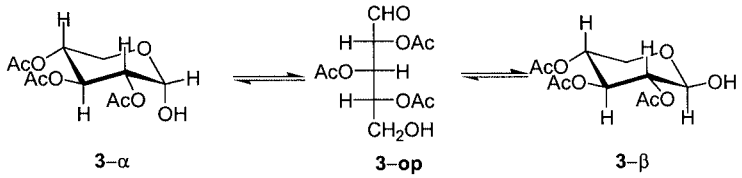


Scheme 2

Table 1. Palladium-catalyzed telomerization of butadiene with protected pyranoses **3** and **6**

Entry[a]	Sugar mmol	C_4H_6 mL [equiv.]	Cat[b] mol %	Time h	Yield[c] [%]	Selectivity [%] l (**α**, **β**)	b (**α**, **β**)	Total **α/β**[d]	Total l/b[e]
	3					**4α**, **4β**	**5α**, **5β**		
1	3.5	3.0 (10)	2	1.5	31	44, 43	8, 5	52:48	87:13 (6.7:1)
2	3.5	13.6 (45)	2	1.5	96	42, 35	15, 8	57:43	77:23 (3.3:1)
3	14	12.0 (10)	2	1.5	58	40, 36	15, 9	55:45	76:24 (3.2:1)
4	3.5	3.0 (10)	1	7	8	44, 43	8, 5	52:48	87:13 (6.7:1)
5	0.85	4.5 (60)	3	3	53	50, 36	9, 5	59:41	86:14 (6.1:1)
	6					**7α**, **7β**	**8α**, **8β**		
5	0.85	4.5 (60)	3	3	72	23, 64	7, 6	30:70	87:13 (6.7:1)
6	3.5	6.0 (20)	2	7	85	26, 63	5, 6	31:69	89:11 (8.1:1)

[a] The reactions were carried out in 4 mL of DMF (except for entry 3, 16 mL), at 75 °C in a 50 mL stainless steel autoclave reactor. [b] The $Pd(acac)_2/2PPh_3$ catalyst system was used. [c] Total yield of telomers based on starting sugar and determined by GC [(**4α**) + (**5α**) + (**4β**) + (**5β**)]. [d] GC ratio (**4α**) + (**5α**)/(**4β**) + (**5β**). [e] GC ratio (**4α**) + (**4β**)/(**5α**) + (**5β**).



Scheme 3

It is interesting to note that none of telomers arising from the open tautomer (**3-op**) (perhaps because of its low concentration in solution[36]) were detected in spite of its two reactive sites (primary hydroxyl and carbaldehyde groups[5−7]).

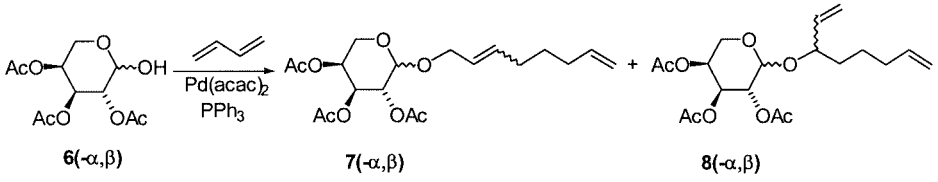
Surprisingly, branched isomers **5α** and **5β** were formed in significant amounts, when compared to the results with methanol as nucleophile leading to minor quantities of **2**. Thus, when the quantitative conversion of starting material **3** was achieved, the ratios of l/b (linear/branched) isomers [**4α**]/[**5α**] and [**4β**]/[**5β**] were as high as 3.0:1 and 4.3:1 respectively (Table 1, entry 3). It is noteworthy that these ratios were dependent on the experimental conditions (Table 1, entries 1−4).

Analogous results were observed starting from L-arabino derivative **6** (Scheme 4). The expected chain isomers **7** and **8** were identified, the amount of branched **8** being again significant (Table 1, entries 5, 6). from this substrate, the β-anomer derivatives are the major compounds.

These results prompted us to study this telomerization in some detail in order to understand the main factors affecting the regioselectivity of the octadienyl chain grafting and to gain some insight into the mechanism of the reaction.

The regiocontrol in the telomerization reaction of butadiene with a nucleophile was unclear for a long time; various mechanistic schemes have been proposed and reviewed.[6,7,12] For the telomerization of butadiene with methanol, a monometallic mechanism (Figure 1) was experimentally proven by Jolly[37,38] and substantiated by recent DFT calculations.[39]

Jolly has proposed that a palladium(0) species induces oxidative coupling of two molecules of butadiene leading to the (η^1,η^3-octadienyl) complex **A**. Protonation by methanol at the C-6 atom of the C_8-chain gives the cationic complex **B**. The attack of methanol or methylate ion at either allylic terminus, C-1 or C-3, results in the formation of the telomers **1** or **2**, respectively. This step determines the regioselectivity of the process and is influenced by experimental



Scheme 4

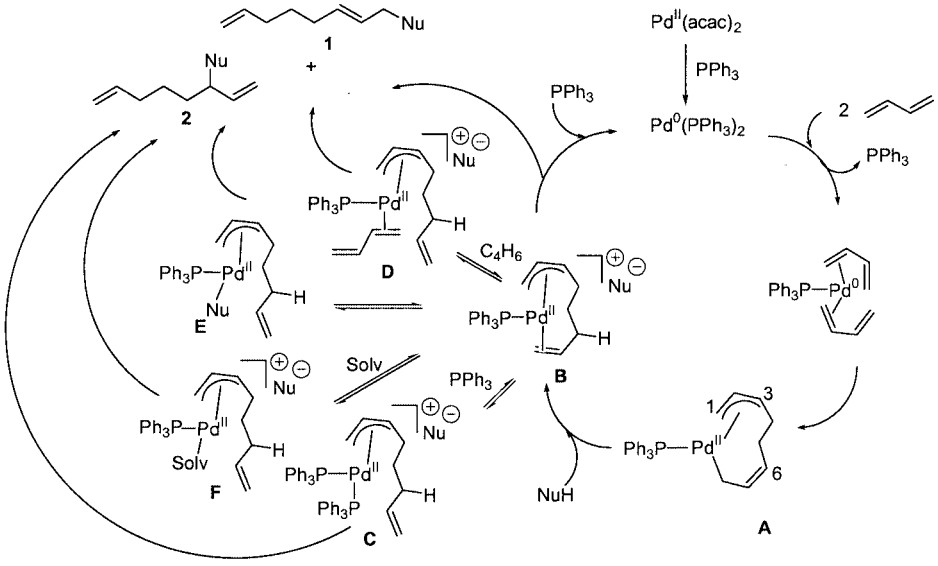


Figure 1. Mechanism of the telomerization

conditions. Recent mechanistic studies of the telomerization of butadiene with methanol[11] and ammonia[40] have completed Jolly's scheme. On the basis of stoichiometric experiments, Beller elegantly disclosed the key role of an internal coordination of the olefinic side chain in the complex **B** in the l/b selective telomer formation.[11] An excess of the coordinating species, phosphane ligand or butadiene favors the formation of η^3-octadienyl-palladium bis(phosphane) complex **C** or η^3-octadienyl-palladium mono(phosphane)-butadiene complex **D**, respectively. The three complexes **B**−**D**, may react with a methylate ion, the regioselectivity of the nucleophilic attack being different for each of them. The overall selectivity therefore depends on the equilibria between **B**, **C**, and **D**. It has been shown that the C-3 position is slightly favored for the attack in complexes **C** and **D** in comparison with complex **B**. According to Beller,[11,41] the formation of the energetically favorable complex **B** with a chelating 1,6-diene ligand results in a nucleophilic attack at the C-1 allylic terminus. Driessen-Hölsher has proposed that an electronic effect of the coordinating ligand in the *trans*-position is responsible for the differentiation between C-1 and C-3 reactivity in complexes **B**, **C**, and **D**.[40] Thus, to achieve good regioselectivity one should avoid a large excess of the phosphane ligand[11,41−43] or butadiene.[11,43]

In considering the l/b isomer ratio, one should also take into account whether the telomerization reaction proceeds under thermodynamic or kinetic control. Telomerization reactions of butadiene with simple alcohols like methanol proceed under kinetic control.[11] On the other hand, the regioselectivity in the reaction of butadiene with phenols is governed by thermodynamic factors.[44−46] Our control experiments revealed that the telomerization of butadiene with **3** is not reversible, since (1) the ratio of isomeric telomers was almost constant throughout the course of the reaction (GC analysis); (2) the composition of the telomer mixtures obtained by fractional distillation did not change if treated with butadiene under reaction conditions.

Some of our results are in agreement with the telomerization mechanism presented in Figure 1. An excess of butadiene resulted in a less selective reaction from **3** (Table 1, entry 2 versus 1 and 4) as early observed with methanol.[11,43] Moreover, even carbohydrate loading had a remarkable effect on the regioselectivity (Table 1, entries 1 and 3 or 2 and 3). As mentioned above, this could be due to a change of butadiene concentration in the liquid phase in the autoclave reactor, when amounts of sugar, butadiene and solvent were simultaneously increased. To better evaluate the effect of sugar concentration on the selectivity, we studied this parameter while keeping constant the amounts of catalyst (3.3%, 2 equivalents PPh_3), butadiene and DMF (Figure 2). If only the butadiene concentration was influencing the selectivity, the best l/b ratio would be expected for the most concentrated solution of **3**, since this corresponds to the lowest butadiene/sugar ratio. In fact, the ratio of l/b telomers increased at first to reach a maximum at 0.44 mol/L of sugar (30 equivalents of butadiene). Evidently, increasing the xylopyranose concentration and diminishing the butadiene/sugar ratio have opposite effects on the regioselectivity of the telomerization. In order to explain the influence of sugar concentration on the regioselectivity, the mechanism of the telomerization reaction has to be completely known. It is possible that the reaction of complex **B** with the nucleophile can interrupt coordination of the olefinic side chain affording complex **E**. Increasing the nucleophile concentration favors the formation of complex **E** and shifts the different equilibria. As a result, the concentration of complex **B** which is responsible for higher selectivity to **4** decreases, inducing a lower regioselectivity.

Next we studied the influence of the phosphane ligand, solvent and temperature as well as the base additive on the

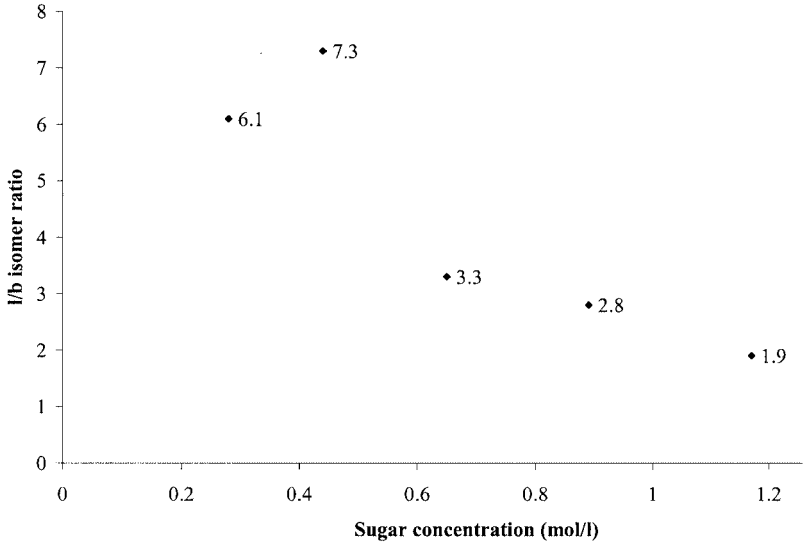


Figure 2. Influence of xylopyranose (**3**) concentration on the ratio linear vs. branched isomers for Pd-catalyzed telomerization of butadiene; reaction conditions: 4.7 mL of butadiene, 4 mL of DMF, 3.3 mol% of $Pd(acac)_2$, 6.6 mol% of PPh_3, 75 °C, 3 h; conversion: 53% (0.24 mol/L), 68% (0.44 mol/L), 81% (0.65 mol/L), 82% (0.89 mol/L), 71% (1.17 mol/L)

course of the telomerization. The effects of various ligands upon the reaction are shown in Table 2. Triphenylphosphane and tri(*p*-tolyl)phosphane gave the most active catalytic systems and provided telomer mixtures with close l/b ratios (entries 1 and 2). Compared to PPh_3, sterically hindered tri(*o*-tolyl)phosphane was less efficient, giving the products in a modest yield, but had a dramatic effect in enhancing the selectivity toward the linear compound (entry 3). The use of tri(*p*-methoxyphenyl)phosphane as well as more basic trialkylphosphanes, such as tri-*n*-butylphosphane or tricyclohexylphosphane, gave no reaction at all (Table 2, entries 6−8), although trialkylphosphanes were suitable with methanol as nucleophile.[47] Likewise the use of the $Pd(OAc)_2$/1,3-dimesitylimidazolin-2-ylidene catalytic system, efficient in telomerization of butadiene with methanol,[48,49] failed in our reaction, since no conversion of **3** was observed.

Table 2. Ligand effect for Pd-catalyzed telomerization of butadiene with **3**

Entry	Ligand	Yield[a] [%]	Selectivity **4α**, **4β** **5α**, **5β**	Total **α**/**β**[b]	Total l/b[c]
1[d]	PPh_3	77	43, 33 15, 9	58:42	76:24 (3.2:1)
2[d]	P(*p*-tol)$_3$	72	42, 32 16, 10	58:42	74:26 (2.8:1)
3[d]	P(*o*-tol)$_3$	26	47, 44 7, 2	54:46	91:9 (10.1:1)
4[e]	P(*o*-tol)$_3$	42	45, 49 4, 2	49:51	94:6 (15.7:1)
5[f]	P(*o*-tol)$_3$	84	45, 48 4, 3	49:51	93:7 (13.3:1)
6[d]	P(*p*-$MeOC_6H_4$)$_3$	1	62, 38 [g]	[g]	[g]
7[d]	PCy_3	4	60, 40 [g]	[g]	[g]
8[d]	P(*n*Bu)$_3$	3	53, 38 5, 4	58:42	91:9 (10.1:1)

[a] Total GC yield of the telomers (**4α** + **5α** + **4β** + **5β**). Isolated yield was 21% in entry 3 (flash chromatography). [b] Ratio: (**4α** + **5α**)/(**4β** + **5β**). [c] Ratio: (**4α** + **4β**)/(**5α** + **5β**). [d] Reaction conditions: 3.5 mmol of **3**, 15 equiv. (4.7 mL) of butadiene, 4 mL of DMF, 0.07 mmol (2 mol %) of $Pd(acac)_2$, 0.14 mmol (4 mol %) of the ligand, 70 °C, 2 h. [e] Reaction conditions: 1.75 mmol of **3**, 30 equiv. (4.7 mL) of butadiene, 2 mL of DMF, 0.035 mmol (2 mol %) of $Pd(acac)_2$, 0.07 mmol (4 mol %) of the ligand, 75 °C, 24 h. [f] Reaction conditions: 1.75 mmol of **3**, 60 equiv. (9.4 mL) of butadiene, 2 mL of DMF, 0.07 mmol (4 mol %) of $Pd(acac)_2$, 0.14 mmol (8 mol %) of P(*o*-tol)$_3$, 70 °C, 24 h. [g] Not determined.

The optimization of the telomer yields was attempted using the most selective $Pd(acac)_2$/P(*o*-tol)$_3$ system. Increasing the butadiene/sugar ratio and the reaction time gave only modest results (Table 2, entries 3, 4). However, using 4 mol% of catalytic system and a large excess of butadiene, we achieved good conversion of xylopyranose (**3**) without loss of regioselectivity (entry 5). It is interesting to note that the influence of butadiene amount on the regioselectivity of the telomerization depends dramatically on the nature of the catalytic system. In contrast to the $Pd(acac)_2$/PPh_3 system (Table 1, entries 1 and 2), an increase in the butadiene amount caused small changes in the l/b telomer ratios when the $Pd(acac)_2$/P(*o*-tol)$_3$ system was employed (Table 2, entries 3−5). The sterically demanding P(*o*-tol)$_3$ appears to prevent the reaction of complex **B** with phosphane, butadiene, or sugar (leading respectively to complexes **C**, **D**, or **E**) and favors the formation of linear isomers through complex **B**.

A comparative study of solvent effect using the $Pd(acac)_2$/PPh_3 catalyst system is reported in Table 3. Hexane, benzene, and toluene are not suitable solvents owing to their low solubilization of xylopyranose. Good yields of telomers were obtained in DMF, acetonitrile, tetrahydrofuran, and dichloromethane, the formation of the linear isomer being favored in THF (entries 1−4). As expected, the selectivity was higher when P(*o*-tol)$_3$ was employed as ligand instead of PPh_3 (entry 5). Under the reaction conditions (4.7 mL of butadiene in 4 mL of the solvent) butadiene is soluble in DMF, acetonitrile, tetrahydrofuran, and dichloromethane even at −10 °C. Nevertheless, changes in the isomer ratios did not correlate with either the solvent dielectric constant or the empirical solvent polarity scale, a parameter recently introduced.[50] As a possible explanation of the selectivity modification by the solvent, we propose that the reaction of complex **B** with a solvent having coordinating properties leads to the loss of internal coordination of the olefinic side chain and provides complex **F** (Scheme 1); an analogous solvent effect was considered by Y. Yamamoto in the amphiphilic allylation via bis-π-allylpalladium complexes.[51]

Table 3. Solvent effect for Pd-catalyzed telomerization of butadiene with **3**

Entry[a]	Solvent	Yield[b] [%]	Products **4α**/**4β**	**5α**/**5β**	Total **α**/**β**[c]	Total l/b[d]
1	DMF	87	43:33	15:9	58:42	76:24 (3.2:1)
2	CH_2Cl_2	98	34:40	14:12	48:52	74:26 (2.6:1)
3	CH_3CN	90	38:42	11:9	49:51	80:20 (4.0:1)
4	THF	97	42:46	7:5	49:51	88:12 (7.3:1)
5[e]	THF	87	39:55	4:2	43:57	94:6 (15.6:1)

[a] Reaction conditions: 3.5 mmol of **3**, 15 equiv. of butadiene (4.7 mL), 2 mol % of $Pd(acac)_2$/2 PPh_3, 4 mL of solvent, 4 h at 70 °C. [b] Total GC yield of the telomers (**4α** + **5α** + **4β** + **5β**). [c] Ratio: (**4α** + **5α**)/(**4β** + **5β**). [d] Ratio: (**4α** + **4β**)/(**5α** + **5β**). [e] $Pd(acac)_2$/2P(*o*-tol)$_3$ as catalyst system, reaction time: 8 h.

It has been shown that a decrease of the temperature led to a higher regioselectivity in the telomerization of butadiene with methanol.[11,47] The results of the temperature effect on the telomerization of butadiene with **3** are reported in Table 4. The catalyst precursor was $Pd_2(dba)_3$·$CHCl_3$ in these experiments, since the reduction of Pd^{II} pre-catalysts may be difficult at low temperature.[11,41] The temperature has a strong influence on the reaction rate. At 20 and 5 °C, good conversions of **3** were obtained after one day; at −10 °C the reaction requires five days and it does not take place at −15 °C (Table 4, entries 1, 3, 5, 7). The correlation of l/b isomer ratio versus temperature is not linear: good selectivity (7.3:1) is observed at 20 °C, this ratio drops to 2.8:1 at 5 °C, but increases to 11.5:1 at −10 °C.

The telomerization reaction is often carried out in the presence of a base as additive.[1,5−7] In the telomerization

Table 4. Effects of temperature and BuLi additive for Pd-catalyzed telomerization of butadiene with **3**

Entry[a]	*T* [°C]	BuLi [equiv.]	Time [d]	Yield[b] [%]	Selectivity **4α/4β**	**5α/5β**	Total **α/β**[c]	Total l/b[d]
1	20	0	1	93	49:39	8:4	57:43	88:12 (7.3:1)
2	20	0.1	1	98	41:54	3:2	44:56	95:5 (19.0:1)
3	5	0	1	96	37:37	19:7	56:44	74:26 (2.8:1)
4	5	0.1	1	90	35:30	24:11	59:41	65:35 (1.9:1)
5	−10[e]	0	4	76	38:53	5:4	41:59	91:9 (10.1:1)
			5	86	37:55	5:3	42:58	92:8 (11.5:1)
6	−10[e]	0.1	4	53	40:55	2.5:2.5	42.5:57.5	95:5 (19.0:1)
			5	73	41:54	2.5:2.5	43.5:56.5	95:5 (19.0:1)
7	−15[e]	0	2	0	−	−	−	−

[a] Reaction conditions: 1.8 mmol of **3**, 30 equiv. of butadiene (4.7 mL), 2.8 mol % of $Pd_2(dba)_3{\cdot}CHCl_3$/2.7 PPh_3, 4 mL of THF in an autoclave reactor. [b] Total GC yield of the telomers (**4α** + **5α** + **4β** + **5β**). [c] Ratio: (**4α** + **5α**)/(**4β** + **5β**). [d] Ratio: (**4α** + **4β**)/(**5α** + **5β**). [e] The reaction was carried out at atmospheric pressure of argon in a Schlenk tube; thus the progress of the reaction could be followed. Combined isolated yield (entries 5, 6) was 74% (flash chromatography).

of butadiene with methanol, Beller has shown that an amine as a base only facilitated the reduction of Pd^{II} pre-catalyst to Pd^0 complexes.[41] The role of the methylate in the same reaction seemed to be dependent on the catalytic system employed; not only the rate of the reaction[52] but also its selectivity[19] was changed in a few cases. Hence we carried out our reaction in the presence of small amounts of *n*BuLi (Table 4, entries 2, 4, 6). A solution of xylopyranose **3** was treated with 0.1 equivalent of BuLi in THF at −78 °C, and then reacted with butadiene in the presence of the $Pd_2(dba)_3{\cdot}CHCl_3/PPh_3$ system in THF at 20, 5, or −10 °C. Compared to the same reactions without base, *n*BuLi influenced the reaction course. At low temperature, the reaction was slower (entries 5 and 6), while the l/b ratios increased at 20 and −10 °C, but decreased at 5 °C. An excellent overall l/b isomer ratio (19:1) was achieved at 20 and −10 °C, the telomerization reaction being remarkably faster at 20 °C.

It is noteworthy that the yield of the linear telomer was higher for the sterically less hindered β-xylopyranose compared to the α-anomer *under all conditions employed*. This fact is astonishing at first sight since the nucleophilic attack at the C-1 atom is favored for steric reasons,[11] and it should therefore predominate for the sterically more hindered α-anomer. Although it is difficult to rationalize these results in view of the complicated mechanism of the telomerization reaction, it seems that the different reactivities of α- and β-anomers affect the selectivity. Taking into consideration that the selectivity of the telomerization reaction is lower when the formation of complexes **C**−**F** is favored, the preferential transformation of **3β** into the linear telomer implies a decreased role of the complexes **C**−**F** in the catalytic cycle. Concerning the anomers' reactivity, a comparison could be attempted. The anomeric composition of **3**, subjected to the telomerization, reached an equilibrium in favor of **3α** under catalysis conditions, even if it varied from one experiment to another (see the above discussion). Since the **α/β**-anomer ratio is lower for the telomers in comparison with the starting mixture, we propose that the **3β**-anomer bearing an equatorial anomeric hydroxyl group in the preferential conformation[53] is more reactive under all conditions employed. An enhanced reactivity of the β-compound was reported for the anomeric *O*-alkylation reaction and explained taking into account kinetic control, thermodynamic anomeric effect,[54] and steric reasons.[55] However our results seem disagree with those of Sinou's group, which did not observe any variation of the anomeric composition during the palladium-catalyzed synthesis of acetylated *O*-glycosides[56] using a Tsuji−Trost reaction. In such a reaction, the π-allyl complex as intermediate exhibits an electrophilic character allowing its attack by the nucleophilic sugar, whereas the bis-π-allyl complex (**A**) in the telomerization, owing to its lowered electrophilic character, undergoes a protonation[37−39] by the same reagent. Thus the rate of mutarotation would be low compared to that of Tsuji−Trost alkylation and high compared to that of telomerization. Furthermore, in our case the **α/β** ratios for the telomers remained close to one in almost all cases. This suggests that the lower reactivity of the α-anomer could be compensated by its more elevated concentration (corresponding to that of the α/β anomeric composition).

Conclusion

In this paper we have described a detailed study of the palladium-catalyzed telomerization of butadiene with *O*-acetylated-pentopyranoses with an insight into the possibility of regiocontrol of the chain grafting. The ratio of linear to branched telomers depends dramatically on the reaction conditions. The monometallic mechanism proposed by Jolly and completed by Beller for the telomerization of butadiene with methanol is capable of rationalizing our results. However, in order to explain the observed influence of the xylopyranose concentration on the regioselectivity, the pathway going through complex **E**, arising in the reaction of monophosphane (η^1,η^3-octadienyl)palladium complex **B** with a nucleophile, has to be taken into consideration. The formation of the analogous complex **F** in the reaction of complex **B** with the solvent is also important. Following a careful optimization of the reaction parameters, a l/b telomers ratio as high as 19:1 was achieved at 20 °C in the presence of the $Pd_2(dba)_3{\cdot}CHCl_3/PPh_3$ system and BuLi. On the other

hand, at elevated temperature, linear telomers (l/b: 13.3:1 in DMF or 15.6:1 in THF) are formed in good yields, when the $Pd(acac)_2/P(o\text{-tol})_3$ catalytic system is used. Thus, C_8-chain glycosides may be obtained in a one-pot procedure starting from readily available and cheap O-acetylated pyranoses and butadiene under mild conditions. Glycosylation methods that employ sugars bearing a free anomeric hydroxyl group are rather few, although they are of particular interest in carbohydrate chemistry for reasons of convenient synthesis.[55] Common approaches are based on a preliminary activation of the sugar molecule by an acid or a base.[57] In transition metal catalytic reactions such an activation is not required, as exemplified in the Tsuji−Trost allylic substitution[56,58] and in the present telomerization reaction.

Experimental Section

General: All experiments were carried out under dry argon using either a 50-mL stainless steel autoclave from Parr Instrument Company or the standard Schlenk technique.

^1H and ^{13}C NMR were recorded on a Bruker AC500 spectrometer (^1H, 500 MHz; ^{13}C, 125.7 MHz) and referenced to TMS. Elemental analyses were carried out on a Perkin−Elmer CHN 2400 instrument. GC analyses were recorded on a Hewlett−Packard HP-6890 gas chromatograph, fitted with a DB-1 capillary column (25 m, 0.32 mm), a flame ionization detector and an HP-3395 integrator. GC/MS spectra were obtained on a Finigan Trace GC 2000 Series Thermoquest spectrometer, fitted with a DB-1 capillary column (25 m, 0.32 mm). Thin-layer chromatography was carried out on Merck, Art 9385, Silica-gel 60 TLC plates.

D-Xylose and L-arabinose, $Pd(acac)_2$, triphenylphosphane, tri(*o*-tolyl)phosphane, tri(*p*-tolyl)phosphane, tri(cyclohexyl)phosphane, tri(*n*-butyl)phosphane, and tri(*p*-methoxyphenyl)phosphane were purchased from Acros Chemical Co and used as received unless otherwise noted. Solvents were distilled under argon: THF from sodium/benzophenone-ketyl; DMF and acetonitrile from CaH_2; CH_2Cl_2 from P_2O_5. All solvents, after drying, were stored on molecular sieves (4 Å), under an inert atmosphere. 1,3-butadiene was flash distilled prior to use. Tri(*n*-butyl)phosphane was distilled under vacuum. Starting compounds prepared as described: $Pd_2(dba)_3{\cdot}CHCl_3$;[59] 1,3- bis(2,4,6-trimethylphenyl)imidazolium chloride;[60] 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene.[61] Peracetylated xylo- and arabinopyranoses[62] were selectively deprotected using hydrazine acetate in DMF[63], leading to 2,3,4-tri-*O*-acetyl-α,β-D-xylopyranose (48%, α/β = 2:1, ^1H NMR, $CDCl_3$, 25 °C) and to 2,3,4-tri-*O*-acetyl-α,β-L-arabinopyranose (40%, α/β = 1/2, ^1H NMR, $CDCl_3$, 25 °C).

Mutarotation of (**3**) and NMR studies, see Table 5.

General Procedure for the Telomerization: $Pd(acac)_2$ and the ligand were charged into a sealed 50-mL stainless steel autoclave. The autoclave was evacuated and filled with argon three times. A DMF solution of the pyranose was transferred under argon from a Schlenk tube into the autoclave. Gaseous 1,3-butadiene was condensed in a Schlenk tube and then transferred into the cooled autoclave. After closing, the autoclave was placed in an oil bath at the required temperature. Stirring was started and continued for the time indicated in Tables 1−4; after cooling, the remaining butadiene was condensed in a Schlenk tube. The conversion and the ratio of isomeric products were determined by GC after acetylation of a sample (0.1 mL) by acetic anhydride (0.2 mL) in the presence of pyridine (0.05 mL) (The mixture was acetylated in order to achieve an adequate GC response from the starting sugar). The telomer mixture was distilled under vacuum (b.p. 124−129 °C, 0.01 mm). Octadienyl 2,3,4-tri-*O*-acetyl-D-xylopyranoside (**4** + **5**): $C_{19}H_{28}O_8$ (384.4) (%): calcd. C 59.36, H 7.34; found C 59.52, H 7.63.

The results of GC analysis are summarized in Tables 1−4. More data are compiled below for the experiment corresponding to Table 2, entry 1. telomers/butadiene dimers: 20:80; the butadiene dimers consist of (*E*)-/(*Z*)-octa-1,3,7-triene/vinylstyrene: 3.5:1, as identified on the basis of their GC/mass spectra; **5α/5β/4α/4β**: 15:9/43:33; the C-3′ epimer ratio was about 40:60 for **5α** and 35:65 for **5β**; that ratio varied from one experiment to another: for example, in Table 4, entry 5, it was 25:75 for **5α**; the *E*-/*Z*-isomer ratio was evaluated to 8:1 for **4α** and **4β** and remained quasi constant whatever the conditions used. The distribution of the linear/branched isomers and α-/β-anomers is given in Tables 1−4.

Separation of the isomers was achieved by successive flash chromatographic separations (petroleum ether/EtOAc, 7:3). The purities of the obtained samples for NMR studies were as follows: **(*E*)-4α**: ≈ 90%; **(*Z*)-4α**: 15% ; **(*E*)-4β**: ≈ 70%; **(*Z*)-4β**: ≈ 60%; **5α**: major epimer: > 90%; minor epimer: > 70%; **5-β**: major epimer: > 50%; minor epimer: > 80%; **(*E*)-7α**: > 95%; **(*Z*)-7α**: 10% ; **(*E*)-7β**: > 95%; **(*Z*)-7β**: ≈ 10%; **8-β**: major epimer: > 90%; minor epimer: > 90%.

Assignments of the signals were based on series of 2D NMR experiments (COSY, HMQC).[64] An assignment of α-/β-isomers was made using spectroscopic data from the corresponding methyl glycosides.[65]

Table 5. Evolution of the **α/β** ratios recorded by ^1H NMR in different conditions

Conditions:[a] Solvent, *T* (K)	5 min	15 min	12 h	36 h
$CDCl_3$, 293	77:23		70:30	66:34
CD_3CN,[b] 293	71:29		62:38	60:40
CD_3CN[b] + HCl, 293	66:34		61:39	
CD_3CN[b] + HCl, 330		60:40		
CD_3CN[b] + HCl, 263		67:33		
CD_3CN[b] + HCl, + butadiene, 261		69:31 (^1H)[c]; 67:33 (^{13}C)		

[a] Starting crystalline form of **3** (α/β = 77:23) was isolated by chromatography. [b] The signal of H_2O was identified in the solvent. [c] The signal of anomeric protons was superimposed with those of butadiene.

Octa-2′,7′-dienyl 2,3,4-Tri-*O*-acetyl-α-D-xylopyranoside (4α). (2*E*)-Isomer: ^{1}H NMR ($CDCl_3$): δ = 1.48 (quint, *J* = 7.5 Hz, 2 H, 5′-H), 1.98−2.12 (m, 4 H, 4′,6′-H), 2.03 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 3.64 (dd, *J* = 10.8 Hz, 10.8 Hz, 1 H, 5-H), 3.77 (dd, *J* = 10.9, 5.9 Hz, 1 H, 5-H), 3.94 (dd, *J* = 12.2, 7.0 Hz, 1 H, 1′-H), 4.12 (dd, *J* = 12.2, 7.0 Hz, 1 H, 1′-H), 4.82 (dd, *J* = 10.1, 3.6 Hz, 1 H, 2-H), 4.92−4.95 (m, 3 H, 8′-H and 4-H), 5.03 (d, *J* = 3.4 Hz, 1 H, 1-H), 5.48−5.53 (m, 1 H, 2′-H), 5.50 (t, *J* = 10.0 Hz, 1 H, 3-H), 5.71 (dt, *J* = 15.4, 6.7 Hz, 1 H, 3′-H), 5.80 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1 H, 7′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.66 (1 C, *C*H_3CO), 20.70 (2 C, *C*H_3CO), 28.06 (C5′), 31.55 (C4′), 33.09 (C6′), 58.27 (C5), 68.27 (C1′), 68.28 (C4), 69.57 (C3), 70.92 (C2), 94.30 (C1), 114.63 (C8′), 125.04 (C3′), 135.40 (C2′), 138.43 (C7′), 169.80 (CH$_3$*C*O), 169.87 (CH$_3$*C*O), 170.02 (CH$_3$*C*O) ppm. MS(CI) *m*/*z*: 402 (8) [M + 18$^+$], 275 (5), 259 (40), 199 (41), 157 (46), 139 (68), 67 (100).

(2*Z*)-Isomer: ^{13}C NMR ($CDCl_3$): δ = 20.66 (1 C, *C*H_3CO), 20.70 (2 C, *C*H_3CO), 26.82 (C4′), 28.52 (C5′), 33.09 (C6′), 58.28 (C5), 64.53 (C1′), 68.28 (C4), 69.58 (C3), 70.92 (C2), 94.54 (C1), 114.72 (C8′), 124.70 (C3′), 134.40 (C2′), 138.43 (C7′), 169.8 (CH$_3$*C*O), 169.87 (CH$_3$*C*O), 170.02 (CH$_3$*C*O) ppm. MS(CI) *m*/*z*: 402 (2) [M + 18$^+$], 275 (2), 259 (30), 199 (25), 157 (35), 139 (45), 97 (48), 82 (61), 67 (100).

Octa-2′,7′-dienyl 2,3,4-Tri-*O*-acetyl-β-D-xylopyranoside (4β). (2*E*)-Isomer: ^{1}H NMR ($CDCl_3$): δ = 1.47 (quint, *J* = 7.4 Hz, 2 H, 5′-H), 2.01−2.12 (m, 4 H, 4′,6′-H), 2.03 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 3.35 (dd, *J* = 11.8, 8.8 Hz, 1 H, 5-H), 4.01 (dd, *J* = 12.2, 6.8 Hz, 1 H, 1′-H), 4.22 (dd, *J* = 12.2, 6.8 Hz, 1 H, 1′-H), 4.11 (dd, *J* = 11.8, 6.7 Hz, 1 H, 5-H), 4.52 (d, *J* = 6.8 Hz, 1 H, 1-H), 4.92 (dd, *J* = 8.5, 6.8 Hz, 1 H, 2-H), 4.92−4.94 (m, 1 H, 4-H), 4.96 (d, *J* = 9.8 Hz, 1 H, 8′-H), 5.00 (d, *J* = 15.2 Hz, 1 H, 8′-H), 5.15 (t, *J* = 8.5 Hz, 1 H, 3-H), 5.48 (dt, *J* = 15.4, 5.6 Hz, 1 H, 2′-H), 5.68 (dt, *J* = 15.4, 6.7 Hz, 1 H, 3′-H), 5.79 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1 H, 7′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.70 (1 C, *C* CO), 20.72 (2C, *C*H_3CO), 28.09 (C5′), 31.54 (C4′), 33.07 (C6′), 61.87 (C5), 68.86 (C4), 69.41 (C1′), 70.72 (C2), 71.39 (C3), 99.10 (C1), 114.62 (C8′), 125.21 (1C3′), 135.02 (C2′), 138.41 (C7′), 169.8 (CH$_3$*C*O), 169.87 (CH$_3$*C*O), 170.02 (CH$_3$*C*O) ppm. MS(CI) *m*/*z*: 402 (3) [M + 18$^+$], 259 (42), 199 (35), 157 (41), 140 (59), 109 (60), 99 (50), 67 (100).

(2*Z*)-Isomer: ^{1}H NMR ($CDCl_3$), only signals which are different in *Z*- and *E*-isomers are given: 4.22 [m, (ABX) 2 H, 1′-H], 5.47 (dt, *J* = 10.0, 6.8 Hz, 1 H, 3′-H), 5.61 (dt, *J* = 10.9, 7.5 Hz, 1 H, 3′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.63 (1C, *C*H_3CO), 20.71 (2C, *C*H_3CO), 26.77 (C4′), 28.50 (C5′), 33.39 (C6′), 61.84 (C5), 64.18 (C1′), 68.72 (C4), 70.66 (C2), 71.34 (C3), 99.20 (C1), 114.42 (C8′), 125.01 (C3′), 135.00 (C2′), 138.38 (C7′), 169.32 (CH$_3$*C*O), 169.75 (CH$_3$*C*O), 170.02 (CH$_3$*C*O) ppm. MS(CI) *m*/*z*: 402 (2) [M + 18$^+$], 275 (3), 259 (29), 199 (25), 157 (34), 139 (45), 109 (33), 97 (46), 82 (61), 67 (100).

Octa-1′,7′-dien-3′-yl 2,3,4-Tri-*O*-acetyl-α-D-xylopyranoside (5α). Major Epimer: ^{1}H NMR ($CDCl_3$): δ = 1.37−1.42 (m, 2 H, 5′-H), 1.41−1.48 (m, 1 H, 4′-H), 1.53−1.59 (m, 1 H, 4′-H), 1.98−2.04 (m, 2 H, 6′-H), 1.99 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 3.65 (dd, *J* = 10.7, 10.7 Hz, 1 H, 5-H), 3.68 (dd, *J* = 10.7, 6.4 Hz, 1 H, 5-H), 3.89 (quint, *J* = 6.2 Hz, 1 H, 3′-H), 4.74 (dd, *J* = 10.2, 3.7 Hz, 1 H, 2-H), 4.89−4.92 (m, 1 H, 4-H), 4.91 (d, *J* = 10.1 Hz, 1 H, 8′-H), 4.96 (d, *J* = 17.1 Hz, 1 H, 8′-H), 5.07 (d, *J* = 3.7 Hz, 1 H, 1-H), 5.09 (d, *J* = 10.7 Hz, 1 H, 1′-H), 5.32 (d, *J* = 17.2 Hz, 1 H, 1′-H), 5.45 (t, *J* = 9.8 Hz, 1 H, 3-H), 5.72 (ddt, *J* = 17.1, 10.1, 7.4 Hz, 1 H, 7′-H), 5.79 (ddd, *J* = 17.2, 10.7, 7.4 Hz, 1 H, 2′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.56 (1 C, *C*H_3CO), 20.61 (1 C, *C*H_3CO), 20.67 (1 C, *C*H_3CO), 23.86 (C5′), 33.43 (C6′), 33.87 (C4′), 58.45 (C5), 69.43 (C4), 69.57 (C3), 71.25 (C2), 80.50 (C3′), 95.06 (C1), 114.68 (C8′), 116.07 (C1′), 138.42 (C7′), 138.58 (C2′), 169.8 (CH$_3$*C*O), 169.87 (CH$_3$*C*O), 170.02 (CH$_3$*C*O) ppm. MS(CI) *m*/*z*: 402 (6) [M + 18$^+$], 275 (5), 259 (29), 199 (25), 157 (30), 139 (45), 109 (33), 67 (100).

Minor Epimer: ^{1}H NMR ($CDCl_3$): δ = 1.37−1.42 (m, 2 H, 5′-H), 1.53−1.57 (m, 1 H, 4′-H), 1.68−1.72 (m, 1 H, 4′-H), 2.02 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 2.06−2.10 (m, 2 H, 6′-H), 3.67 (dd, *J* = 10.8, 10.8 Hz, 1 H, 5-H), 3.77 (dd, *J* = 10.8, 6.7 Hz, 1 H, 5-H), 3.95 (quint, *J* = 6.6 Hz, 1 H, 3′-H), 4.93 (d, *J* = 17.0 Hz, 1 H, 8′-H), 5.01 (d, *J* = 10.2 Hz, 1 H, 8′-H), 4.79 (dd, *J* = 10.2, 3.7 Hz, 1 H, 2-H), 4.93−4.95 (m, 1 H, 4-H), 5.03 (d, *J* = 3.5 Hz, 1 H, 1-H), 5.18 (d, *J* = 17.9 Hz, 1 H, 1′-H), 5.19 (d, *J* = 9.6 Hz, 1 H, 1′-H), 5.48 (t, *J* = 9.9 Hz, 1 H, 3-H), 5.52 (ddt, *J* = 17.2, 10.6, 8.0 Hz, 1 H, 2′-H), 5.81 (ddt, *J* = 17.2, 10.6, 7.4 Hz, 1 H, 7′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.64 (1 C, *C*H_3CO), 20.73 (1 C, *C*H_3CO), 20.76 (1 C, *C*H_3CO), 24.25 (C5′), 33.47 (C6′), 34.62 (C4′), 58.55 (C5), 69.48 (C4), 69.61 (C3), 70.78 (C2), 78.32 (C3′), 92.63 (C1), 114.78 (C8′), 118.59 (C1′), 137.11 (C2′), 138.33 (C7′), 169.8 (CH$_3$*C*O), 169.87 (CH$_3$*C*O), 170.02 (CH$_3$*C*O) ppm. MS(CI) *m*/*z*: 402 (4) [M + 18$^+$], 275 (5), 259 (29), 199 (28), 157 (30), 139 (39), 109 (33), 95 (57), 81(72), 67 (100).

Octa-1′,7′-dien-3′-yl 2,3,4-Tri-*O*-acetyl-β-D-xylopyranoside (5β). Major Epimer: ^{1}H NMR ($CDCl_3$): δ = 1.33−1.50 (m, 2 H, 5′-H), 1.41−1.50 (m, 1 H, 4′-H), 1.51−1.58 (m, 1 H, 4′-H), 1.98−2.04 (m, 2 H, 6′-H), 1.99 (s, 6 H, Ac), 2.03 (s, 3 H, Ac), 3.31 (dd, *J* = 11.7, 8.6 Hz, 1 H, 5-H), 4.03 (quint, *J* = 6.9 Hz, 1 H, 3′-H), 4.06 (dd, *J* = 11.7, 5.0 Hz, 1 H, 5-H), 4.51 (d, *J* = 6.5 Hz, 1 H, 1-H), 4.85 (dd, *J* = 8.1, 6.5 Hz, 1 H, 2-H), 4.88−4.90 (m, 1 H, 4-H), 4.91 (d, *J* = 10.1 Hz, 1 H, 8′-H), 4.98 (d, *J* = 17.1 Hz, 1 H, 8′-H), 5.03 (t, *J* = 8.1 Hz, 1 H, 3-H), 5.15 (d, *J* = 16.3 Hz, 1 H, 1′-H), 5.17 (d, *J* = 9.7 Hz, 1 H, 1′-H), 5.53 (ddd, *J* = 17.2, 9.8, 8.0 Hz, 1 H, 2′-H), 5.74 (ddt, *J* = 17.3, 10.6, 7.4 Hz, 1 H, 7′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.59 (1 C, *C*H_3CO), 20.63 (2 C, *C*H_3CO), 24.23 (C5′), 33.36 (C6′), 34.55 (C4′), 61.48 (C5), 68.69 (C4), 70.49 (C2), 71.01 (C3), 78.45 (C3′), 96.98 (C1), 114.57 (C8′), 117.94 (C1′), 137.28 (C7′), 138.35 (C2′), 169.63 (CH$_3$*C*O), 169.83 (CH$_3$*C*O), 170.06 (CH$_3$*C*O) ppm. MS(CI) *m*/*z*: 402 (2) [M + 18$^+$], 259 (39), 199 (33), 157 (32), 139 (45), 109 (40), 97(54), 81(66), 67 (100).

Minor Epimer: ^{1}H NMR ($CDCl_3$): δ = 1.35−1.45 (m, 2 H, 5′-H), 1.43−1.55 (m, 1 H, 4′-H), 1.58−1.67 (m, 1 H, 4′-H), 2.01−2.07 (m, 2 H, 6′-H), 2.03 (s, 6 H, Ac), 2.04 (s, 3 H, Ac), 3.34 (dd, *J* = 11.8, 9.2 Hz, 1 H, 5-H), 3.98 (quint, *J* = 6.7 Hz, 1 H, 3′-H), 4.09 (dd, *J* = 11.8, 5.2 Hz, 1 H, 5-H), 4.53 (d, *J* = 7.0 Hz, 1 H, 1-H), 4.93 (dd, *J* = 8.8, 7.0 Hz, 1 H, 2-H), 4.95−4.97 (m, 1 H, 4-H), 4.97 (d, *J* = 10.1 Hz, 1 H, 8′-H), 4.99 (d, *J* = 17.1 Hz, 1 H, 8′-H), 5.11 (d, *J* = 10.5 Hz, 1 H, 1′-H), 5.16 (t, *J* = 8.8 Hz, 1 H, 3-H), 5.20 (d, *J* = 17.2 Hz, 1 H, 1′-H), 5.77 (ddt, *J* = 17.3, 10.6, 6.9 Hz, 1 H, 7′-H), 5.81 (ddd, *J* = 17.3, 10.4, 7.0 Hz, 1 H, 2′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.71 (3 C, *C*H_3CO), 24.02 (C5′), 33.48 (C6′), 34.19 (C4′), 62.07 (C5), 68.83 (C4), 71.15 (C2), 71.68 (C3), 81.89 (C3′), 100.11 (C1), 114.65 (C8′), 115.84 (C1′), 138.32 (C7′), 138.70 (C2′), 169.30 (CH$_3$*C*O), 169.79 (CH$_3$*C*O), 170.19 (CH$_3$*C*O) ppm. MS(CI) *m*/*z*: 402 (2) [M + 18$^+$], 259 (33), 199 (26), 157 (30), 139 (39), 95(55), 81(78), 67 (100).

(2′-*E*)-Octa-2′,7′-dien-1′-yl 2,3,4-Tri-*O*-acetyl-α-L-arabinopyranoside (7α): ^{1}H NMR ($CDCl_3$): δ = 1.47 (quint, *J* = 7.6 Hz, 2 H, 5′-H), 2.01−2.12 (m, 4 H, 4′,6′-H), 2.01 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 2.12 (s, 3 H, Ac), 3.60 (dd, *J* = 13.0, 1.6 Hz, 1 H, 5-H), 4.01 (dd, *J* = 13.0, 3.0 Hz, 1 H, 5-H), 4.03 (dd, *J* = 12.0, 6.8 Hz, 1 H, 1′-H), 4.25 (dd, *J* = 12.0, 5.5 Hz, 1 H, 1′-H), 4.45 (d, *J* = 7.0 Hz,

1 H, 1-H), 4.95−4.97 (m, 2 H, 8′-H), 5.02 (dd, J = 9.4, 2.5 Hz, 1 H, 3-H), 5.19 (dd, J = 9.4, 7.0 Hz,, 1 H, 2-H), 5.23−5.25 (m, 1 H, 4-H), 5.48 (dt, J = 15.3, 6.8 Hz, 1 H, 2′-H), 5.68 (dt, J = 15.3, 6.8 Hz, 1 H, 3′-H), 5.78 (ddt, J = 17.0, 10.0, 6.7 Hz, 1 H, 7′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.64 (1 C, CH_3CO), 20.75 (1 C, CH_3CO), 20.89 (1 C, CH_3CO), 28.11 (C5′), 31.55 (C4′), 33.09 (C6′), 63.06 (C5), 67.67 (C4), 69.12 (C2), 69.50 (C1′), 70.19 (C3), 99.43 (C1), 114.63 (C8′), 125.27 (C3′), 134.94 (C2′), 138.43 (C7′), 169.42 (CH_3CO), 170.15 (CH_3CO), 170.32 (CH_3CO) ppm. MS(CI) m/z: 402 (80) [M + 18$^+$], 294 (5), 259 (100), 217 (12), 141 (17), 109 (35), 60 (50).

Octa-2′,7′-dien-1′-yl 2,3,4-Tri-*O*-acetyl-β-L-arabinopyranoside (7β): MS(CI) m/z: 402 (69) [M + 18$^+$], 294 (4), 259 (100), 217 (12), 139 (16), 60 (35).

(2′-*E*)-Isomer: ^{1}H NMR ($CDCl_3$): δ = 1.47 (quint, J = 7.5 Hz, 2 H, 5′-H), 2.01−2.12 (m, 4 H, 4′,6′-H), 1.99 (s, 3 H, Ac), 2.07 (s, 3 H, Ac), 2.13 (s, 3 H, Ac), 3.65 (dd, J = 13.0, 1.9 Hz, 1 H, 5-H), 3.93 (ddd, J = 12.2, 6.9, 1.0 Hz, 1 H, 1′-H), 3.97 (dd, J = 13.0, 1.2 Hz, 1 H, 5-H), 4.11 (ddd, J = 12.2, 5.7, 1.0 Hz, 1 H, 1′-H), 4.95 (dm, J = 10.2 Hz, 1 H, 8′-H), 4.99 (dm, J = 18.7 Hz, 1 H, 8′-H), 5.10 (d, J = 3.6 Hz, 1 H, 1-H), 5.17 (dd, J = 10.5, 3.5 Hz, 1 H, 2-H), 5.31−5.33 (m, 1 H, 4-H), 5.35 (dd, J = 10.5, 3.5 Hz, 1 H, 3-H), 5.48 (dt, J = 15.4, 6.8 Hz, 1 H, 2′-H), 5.69 (dt, J = 15.4, 6.8 Hz, 1 H, 3′-H), 5.78 (ddt, J = 17.0, 10.2, 6.7 Hz, 1 H, 7′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.16 (1 C, CH_3CO), 21.27 (1 C, CH_3CO), 21.40 (1 C, CH_3CO), 28.55 (C5′), 32.06 (C4′), 33.59 (C6′), 60.83 (C5), 67.67 (C4), 68.75 (C2), 68.85 (C1′), 69.63 (C3), 95.51 (C1), 115.22 (C8′), 125.52 (C3′), 135.92 (C2′), 138.92 (C7′), 170.48 (CH_3CO), 170.81 (CH_3CO), 170.86 (CH_3CO).

(2′-*Z*)-Isomer: ^{13}C NMR ($CDCl_3$): δ = 21.16 (1 C, CH_3CO), 21.27 (1 C, CH_3CO), 21.40 (1 C, CH_3CO), 27.31 (C4′), 29.02 (C5′), 33.59 (C6′), 60.83 (C5), 67.67 (C4), 68.75 (C2), 63.67 (C1′), 69.63 (C3), 95.68 (C1), 115.28 (C8′), 125.16 (C3′), 135.00 (C2′), 138.92 (C7′), 170.48 (CH_3CO), 170.81 (CH_3CO), 170.86 (CH_3CO).

Octa-1′,7′-dien-3′-yl 2,3,4-Tri-*O*-acetyl-α-L-arabinopyranoside (8α). Major Epimer: MS(CI) m/z: 402 (9) [M + 18$^+$], 259 (16), 217 (6), 144 (8), 126 (24), 77 (43), 60 (95), 44 (100).

Minor Epimer: MS(CI) m/z: 402 (3) [M + 18$^+$], 259 (4), 217 (5), 144 (4), 126 (15), 77 (18), 60 (43), 44 (100).

1 Octa-1,7-dien-3-yl 2,3,4-Tri-*O*-acetyl-β-L-arabinopyranoside (8β): MS(CI) m/z: 402 (8) [M + 18$^+$], 259 (19), 217 (5), 141 (9), 126 (21), 77 (48), 60 (100), 44 (62).

Major Epimer: ^{1}H NMR ($CDCl_3$): δ = 1.35−1.45 (m, 2 H, 5′-H), 1.45−1.58 (m, 2 H, 4′-H), 2.04−2.12 (m, 2 H, 6′-H), 2.01 (s, 3 H, Ac), 2.07 (s, 3 H, Ac), 2.13 (s, 3 H, Ac), 3.60 (dd, J = 13.0, 1.9 Hz, 1 H, 5-H), 3.95 (dd, J = 13.0, 6.3 Hz, 1 H, 5-H), 4.12 (quint, J = 7.1 Hz, 1 H, 3′-H), 4.97 (d, J = 10.0 Hz, 1 H, 8′-H), 5.01 (d, J = 17.1 Hz, 1 H, 8′-H), 5.13 (d, J = 10.1 Hz, 1 H, 1′-H), 5.14 (dd, J = 10.5, 3.5 Hz, 1 H, 2-H), 5.17 (d, J = 3.6 Hz, 1 H, 1-H), 5.19 (d, J = 15.2 Hz, 1 H, 1′-H), 5.35 (dd, J = 10.5, 3.5 Hz, 1 H, 3-H), 5.33−5.35 (m, 1 H, 4-H), 5.78 (ddt, J = 17.2, 10.7, J = 7.4 Hz, 1 H, 7′-H), 5.85 (ddd, J = 17.2, 10.7, 7.4 Hz, 1 H, 2′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.78 (CH_3CO), 20.82 (CH_3CO), 20.95 (CH_3CO), 23.98 (C5′), 33.49 (C6′), 33.98 (C4′), 60.62 (C5), 67.29 (C4), 68.72 (C2), 69.23 (C3), 80.47 (C3′), 95.86 (C1), 114.78 (C8′), 116.19 [C(1′), 138.36 [C(7′), 138.52 (C2′), 170.12 (CH_3CO), 170.42 (2C, (CH_3CO).

Minor Epimer: ^{1}H NMR ($CDCl_3$): δ = 1.35−1.45 (m, 2 H, 5′-H), 1.45−1.58 (m, 2 H, 4′-H), 2.04−2.12 (m, 2 H, 6′-H), 2.00 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 2.14 (s, 3 H, Ac), 3.67 (dd, J = 10.0, 1.8 Hz, 1 H, 5-H), 3.94 (dd, J = 13.0, 6.3 Hz, 1 H, 5-H), 4.99 (quint, J = 7.1 Hz, 1 H, 3′-H), 4.98 (d, J = 10.0 Hz, 1 H, 8′-H), 4.99 (d, J = 15.5 Hz, 1 H, 8′-H), 5.10−5.21 (m, 4 H, H1,2,1′), 5.33−5.35 (m, 2 H, H3,4), 5.54 (ddd, J = 18.5, 10.4, 8.1 Hz, 1 H, 2′-H), 5.74 (m, 1 H, 7′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.48 (CH_3CO), 20.64 (CH_3CO), 20.75 (CH_3CO), 24.68 (C5′), 33.35 (C6′), 34.66 (C4′), 60.39 (C5), 67.24 (C4), 68.31 (C2), 69.20 (C3), 78.19 (C3′), 93.32 (C1), 114.88 (C8′), 118.57 (C1′), 137.16 (C2′), 138.61 (C7′), 170.12 (CH_3CO), 170.24 (CH_3CO), 170.42 (CH_3CO).

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