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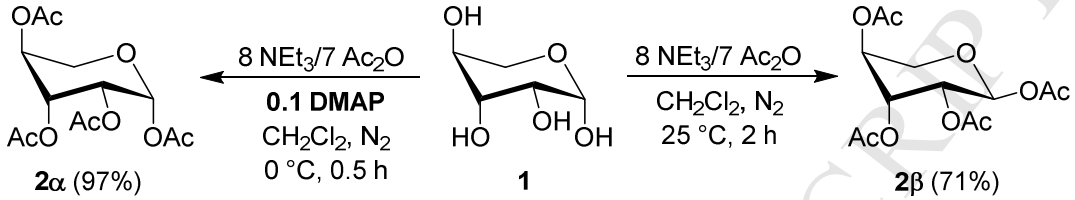
Graphical Abstract



Stereoselective Acetylation of Hemicellulosic C5-Sugars

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Abstract

The stereoselective peracetylation of α-D-xylose (**1**) and α-L-arabinose (**4**) using a combination of triethylamine and acetic anhydride in the presence or absence of a catalytic amount of dimethylaminopyridine (DMAP) is described. The peracetylated D-xylose and L-arabinose alpha pyranose anomers **2α** and **5α** are obtained in 97 % and 56 % yields respectively. The peracetylated D-xylose beta pyranose anomer **2β** is obtained in 71 % yield through simple modification of the reaction conditions. Details regarding synthesis and isolation optimization studies under different conditions are presented below. The stereoselective peracetylation reactions disclosed here have been used to separate mixtures of D-xylose and L-arabinose as their peracetylated derivatives **2β** and **5α** in 47 % and 42 % yields and can provide pure pentoses after deacetylation.

Keywords

acetylation; stereoselective; carbohydrate; pentoses; xylose; arabinose

Introduction

The growing importance of carbohydrates in the synthesis of value-added chemicals,[1,2,3] conversion to biofuels,[4] and the understanding of their importance to a multitude of biological processes[5] has led to an increase in research efforts for new, practical, and stereoselective methods for the synthesis of carbohydrate derivatives. While much attention has focused on the use of C6-sugars (hexoses) derived from cellulose[6], less attention has been paid to derivatization and use of C5-sugars (pentoses) obtained from hemicellulose rich biomass.[7] Acetylation is one of the most common reactions in carbohydrate chemistry since it provides an efficient method for the conversion of hydrophilic hydroxyl groups to hydrophobic acetate functionalities that are more soluble in organic solvents. A common route used for the peracetylation of sugars with acetic anhydride requires pyridine as both the solvent and base for the acetylation reaction despite its unpleasant odor and known toxicity.[8] While the yields are acceptable, the presence of a mixture of regioisomers (pyranose and furanose) as well as anomers (α- and β-) makes this reaction less than desirable when a single well-defined stereochemical product is preferred. Addition of 4-(*N*,*N*)-dimethylaminopyridine (DMAP), as a co-catalyst increases the rate of the acetylation, reaction but does not lead to a change in the stereochemical outcome of the reaction.[9] The solvent free peracetylation of various mono- and disaccharides using a catalytic amount of iodine in neat acetic anhydride was disclosed in 2004.[10] The method is operationally simple, leads to exclusive formation of the peracetylated sugars as their pyranosyl esters in high yields (> 90%), and results in favorable α:β anomer ratios (10:1 or higher) in the case of several C6 mono- and disaccharides. For the C5-sugars, D-xylose and L-arabinose, while the peracetylated product yields are high the α:β anomer ratios are lower (4:1 for D-xylose) as well as opposite for the two C5 sugars (1:3 α:β ratio for L-arabinose). The use of anhydrous sodium acetate in refluxing acetic anhydride,[11] which forms the β-glycosyl acetate in good yield, is the only known stereoselective acetylation reaction. Unfortunately, this method is not synthetically useful if the α-glycosyl acetate is the desired product. Numerous other methods for the peracetylation of carbohydrates exist in the literature,[12-13] each with its own advantages and

disadvantages, but none of these methods lead to the stereoselective formation of the β-glycosyl acetate versus α-glycosyl acetate through simple modification of the reaction conditions. Therefore, there still is a need for a general procedure for the steroselective peracetylation of carbohydrates.

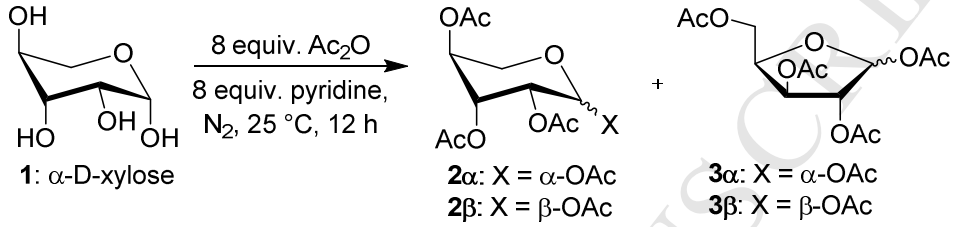
Hemicellulose based sugars (e.g., D-xylose and L-arabinose) can provide a platform for synthesis of a variety of industrially important chemicals that are currently derived from petroleum. At the beginning of the bio-refinery process, hemicellulose rich biomass is selectively extracted to produce a C-5 sugar rich hydrolyzate.[14] Crystalline D-xylose and L-arabinose are isolated, as their pyranose regioisomers, from the pentose rich hydrolysate using a boronic acid mediated methodology.[15] This two-step process provides a mixture of the two, pure, monosaccharides required for subsequent synthetic transformations with the first step often being the peracetylation of the isolated C-5 sugar. The classic pyridine based peracetylation protocol[8] was initially used, but there were several drawbacks. The long reaction time (12 hrs), low yield of the α-pyranose peracetylated C5-sugar which we desired for further synthetic manipulations, and inability to isolate pure product made the use of this methodology far from desirable for our integrated bio-refinery. Optimization of this step, in terms of both stereoselectivity and our desire to use greener reaction conditions, was critical to make the overall process cost effective and sustainable within our integrated bio-refinery. We describe herein the stereoselective peracetylation of D-xylose and L-arabinose using a combination of triethylamine and acetic anhydride in the presence or absence of a catalytic amount of DMAP. The desired alpha or beta pyranosyl esters are obtained in high yield and purity through simple modification of the reaction conditions. Synthesis and isolation optimization studies follow.

Results and Discussions

Peracetylation using Neat Pyridine. We sought to develop a methodology whereby C5-sugars, primarily D-xylose and L-arabinose, could be peracetylated in a stereoselective fashion where simple modification of the reaction conditions led to the formation of the α-pyranoid or β-pyranoid hemiacetal anomers in high yield and purity. We began by examining the product distribution from the

peracetylation of both C5-sugars using the known pyridine/acetic anhydride methodology. Peracetylation of α-D-xylopyranose (**1**), whose full ^{1}H and ^{13}C NMR characterization can be found in the general experimental section, was carried out using the method of Shindo (Scheme 1).[16] To a white suspension of **1** in neat pyridine, acetic anhydride

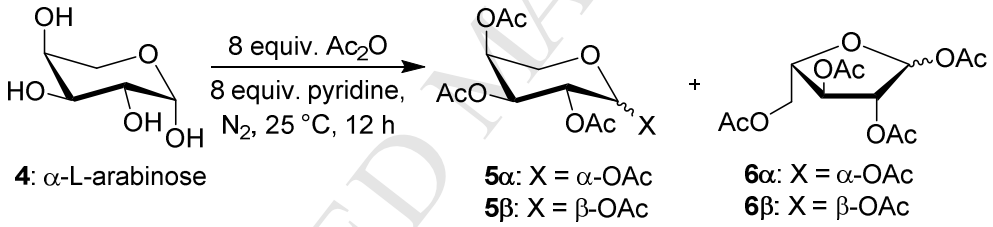
Scheme 1



was added over the course of several minutes at 25 ˚C and then the reaction was allowed to stir under N_2. Within 15 minutes of stirring, the reaction mixture had turned clear and golden in appearance. After stirring for 12 hours at 25 ˚C, the clear golden solution was subjected to an aqueous workup (see experimental section) and the resulting isolated yellow oil characterized by ^{1}H NMR. The results are shown in Table 1 (entries 1 and 2). The overall yield of the peracetylation reaction was near quantitative, but multiple products were observed. ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed the yellow oil was comprised of two regioisomers, tetraacetylated D-xylopyranose (TXP) **2** and tetraacetylated D-xylofuranose (TXF) **3**, in a ratio of 94:6. For both regioisomers **2** and **3** there also existed α- and β-anomers. The ratio of TXP anomers was **2α**:**2β** = 6:4 and the TXF anomers was **3α**:**3β** = 1:1. Chemical shift assignments for the four TXP and TXF anomers were made via comparison with literature values for **2α**,[17] **2β**,[18] and **3α**/**3β**.[19] Relative ratios of the four products were determined by comparing C(1)-H integral values of each anomer located at δ 6.42 ppm (doublet, TXF **3α**), δ 6.21 ppm (doublet, TXP **2α**), δ 6.11 ppm (singlet, TXF **3β**), and δ 5.71 ppm (doublet, TXP **2β**) in the low field region of the ^{1}H NMR . Observation of four compounds in the isolated product mixture came as a surprise since we could find no mention of the presence of furanose isomers **3α**/**3β** in the published literature (Table 1, entries 1 and 2).[16, 18]

The pyridine/acetic anhydride peracetylation method was also examined using α-L-arabinose (**4**), which was also characterized by ^{1}H and ^{13}C NMR (see general experimental section), since **4** can be obtained from the hemicellulose derived, pentose rich hydrolyzate.[15] Peracetylation of **4** was carried out using the method of Jakeman (Scheme 2). To a white suspension of **4** in neat pyridine, acetic anhydride was added over the course of several minutes at 25 ˚C and then the suspension was allowed to stir under N_2. After stirring for 12 hours at 25 ˚C, the clear golden solution was subjected to an aqueous workup (see experimental section) and the resulting isolated yellow oil characterized by ^{1}H NMR. The results are shown in Table 1 (entries 3 and 4). The overall yield of the peracetylation **4** was near quantitative but multiple products were identified as was observed for peracetylated α-D-xylopyranose. ^{1}H NMR characterization of the isolated reaction

Scheme 2



4: α-L-arabinose

5α: X = α-OAc
5β: X = β-OAc

6α: X = α-OAc
6β: X = β-OAc

mixture in $CDCl_3$ showed the yellow oil was comprised of two regioisomers, tetraacetylated L-arabinopyranose (TAP) **5** and tetraacetylated L-arabinofuranose (TAF) **6**, in a ratio of 75:25. For both of the regioisomers, **5** and **6**, there also existed α- and β-anomers. The ratio of TAP anomers was **5α**:**5β** = 6:4 and the TAF anomers was **6α**:**6β** = 4:6. Chemical shift assignments for the four TAP and TAF anomers were made via comparison with literature values for **5α**/**5β**,[20] and **6α**/**6β**.[21] Relative ratios of the four products were determined by comparing C(1)-H integral values of each anomer located at δ 6.37 ppm (doublet, TAF **6α**), δ 6.34 ppm (doublet, TAP **5α**), δ 6.19 ppm (singlet, TAF **6β**), and δ 5.64 ppm (doublet, TAP **5β**) in the low field region of the ^{1}H NMR . As with the peracetylation of α-D-xylopyranose, the observation of four compounds in the isolated product mixture was unexpected,

especially with such a large proportion of **6α**/**6β** present, since only the presence of the pyranose products **5α** and **5β** are described in the literature.[9, 20]

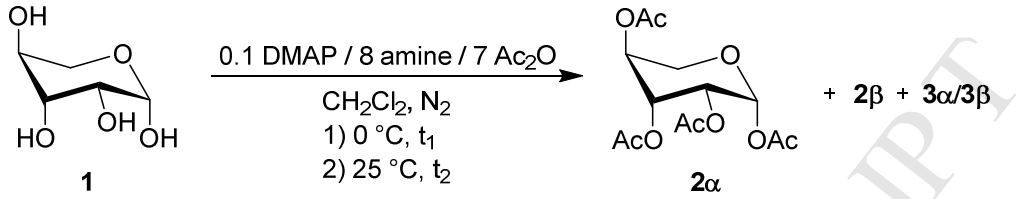
Table 1. Peracetylation of C5 sugars in neat pyridine

				peracetylated C5 sugars[b]					
				hemiacetal ratio[c]		anomer ratio[d]			
entry	C5 sugar	acetylated product	yield (%)[a]	pyranose	furanose	α_p	β_p	α_f	β_f
1	α-D-Xyl (**1**)	**2** / **3**	100	94	6	60	40	50	50
2	α-D-Xyl (**1**)	**2** / **3**	100	95	5	68	32	57	43
3	α-L-Ara (**4**)	**5** / **6**	100	73	27	60	40	40	60
4	α-L-Ara (**4**)	**5** / **6**	100	75	25	60	40	40	60

[a]based on mass of all peracetylated C5 sugars present in isolated reaction mixture. [b]pyranose/furanose and anomer ratios determined by ^{1}H NMR of the reaction mixture after workup. [c]pyranose = $\alpha_p + \beta_p$; furanose = $\alpha_f + \beta_f$. [d]p = pyranose; f = furanose.

Peracetylation in Presence of DMAP/Amine. The product regiochemistry and lack of stereochemical control observed in our initial peracetylation reactions led us to explore alternative conditions that would allow for the isolation of an anomerically pure pyranose product in high yield. Our idea was to optimize the peracetylation reaction by making the reaction more atom economic, decreasing the reaction time, and using greener reagents where possible. The use and amount of pyridine required in these reactions was not acceptable as pyridine is a harmful, noxious chemical that is environmentally detrimental and harmful to human health. We decided to evaluate the use of triethylamine (NEt_3) as a greener alternative to pyridine in these reactions.[22] Use of NEt_3 for the peracetylation of glucose, xylose, and rhamnose was disclosed in 2000[23] as a footnote in a table but no indication of the reaction's stereochemical outcome was discussed. Furthermore, no actual experimental details were given in the text of the paper nor the accompanying supporting information. Based on this initial literature lead, we explored the peracetylation of **1** to form **2α** (Scheme 3). Acetic anhydride was added to a CH_2Cl_2

Scheme 3



suspension that contained **1** (10.0 g, 66.6 mmol), eight equivalents of NEt_3, and a catalytic amount of DMAP cooled to 0 ˚C. After one hour of stirring at 0 ˚C, the reaction mixture was clear and orange in color. The reaction was stirred at 25 ˚C for 19 hours, subjected to an aqueous workup (see experimental section), a viscous orange oil was isolated and assessed using ^{1}H NMR. The results are shown in Table 2 (entry 9). As observed previously with neat pyridine, the peracetylation yield was quantitative. Gratifyingly, our acetylation reaction conditions yielded excellent regio- and stereochemical results as well. The isolated orange oil consisted of tetraacetylated D-xylopyranoses **2α**, characterized by a doublet at δ 6.21 ppm (J = 4.0, equatorial C(1)-H), and **2β**, characterized by the doublet at δ 5.71 ppm (J = 6.8, axial C(1)-H), in a 94:6 ratio of the two anomers. The furanose steroisomers **3α** and **3β** were not present in the isolated oil. This result was in stark contrast to the peracetylation of **1** in neat pyridine where formation of tetraacetylated xylopyranoses **2α** and **2β** was favored but a 60:40 mixture of anomers prevented the isolation of either. With this very encouraging result in hand, we sought to optimize the reaction conditions further towards the exclusive formation of **2α**.

Table 2. Peracetylation of α-D-xylose (**1**) in the presence of DMAP/amine[a]

					peracetylated D-xylose[c]					
					hemiacetal ratio[d]		anomer ratio[e]			
entry	amine	0 ˚C, t_1 (h)	25 ˚C, t_2 (h)	yield (%)[b]	2α/β	3α/β	2α	2β	3α	3β
1	NEt_3	1	4	99	100	-	98	2	-	-
2	NEt_3	1	4	81	100	-	98	2	-	-
3	NEt_3	0.5	2	94	100	-	98	2	-	-
4	NEt_3	0.5	0.5	100	100	-	98	2	-	-
5	NEt_3	0.5	0.5	99	100	-	98	2	-	-
6	NEt_3	0.5	-	99	100	-	98	2	-	-
7	NEt_3	-	2.5	87	93	7	72	28	50	50
8	pyridine	1	2	97	100	-	99	1	-	-
9[f]	NEt_3	1	19	100	100	-	94	6	-	-

[a]Conditions: α-D-xylose (2 g, 13 mmol, 1 equiv), DMAP (10 mol %), amine (8 equiv), and Ac_2O (7 equiv) reacted in CH_2Cl_2 (10 mL) at indicated temperatures for indicated time. [b]based on mass of all peracetylated C5 sugars present in isolated reaction mixture. [c]pyranose/furanose and anomer ratios determined by ^1H NMR of the reaction mixture after workup. [d]pyranose = $\alpha_p + \beta_p$; furanose = $\alpha_f + \beta_f$. [e]p = pyranose; f = furanose. [f]large scale peracetylation: α-D-xylose (10.0 g, 66.6 mmol, 1 equiv), DMAP (10 mol %), amine (8 equiv), and Ac_2O (7 equiv) reacted in CH_2Cl_2 (50 mL) at indicated temperatures for indicated time.

In an effort to streamline the reaction conditions, we first explored the length of time required for the reaction to stir at 25 ˚C after the addition of acetic anhydride at 0 ˚C. Our hope was to maintain the high product selectivity for the formation of **2α** observed in our first experiment and considerably shorten the time required, thus making our reactions more efficient. The effect of time at 25 ˚C on yield as well as regiochemistry/stereochemistry was evaluated by performing the peracetylation of **1** (2 g, 13 mmol) at 0 ˚C then allowing the reaction to stir for different lengths of time (4, 2, 0.5 hours) at 25 ˚C followed by aqueous work-up and isolation (Table 2, entries 1-5). Assessment of each isolated reaction mixture by ^1H NMR showed that regardless of the time the reaction was allowed to stir at 25 ˚C the peracetylation yield of **1** was high with only TXP anomers **2α** and **2β** present. Next, we investigated shortening the time the reaction was stirred at 0 ˚C. We had observed that the white CH_2Cl_2 suspension dissolved completely within 30 minutes at 0 ˚C to yield a clear, pale yellow solution after the addition of acetic anhydride was complete. When we allowed the reaction to only stir for 30 minutes at 0 ˚C, complete dissolution of the

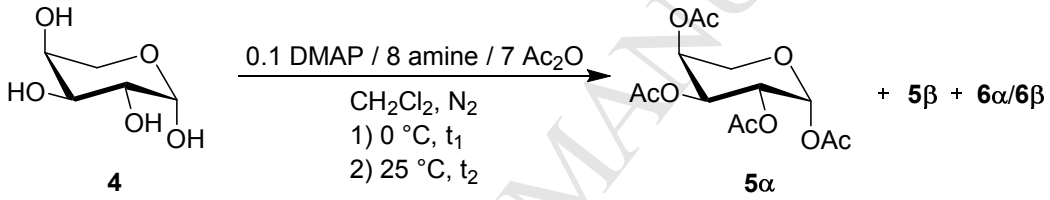
reactants was observed in each case and no change in the conversion of **1** and product distribution of the TXP anomers **2α** and **2β** was observed (Table 2, entries 3-5). If the addition of acetic anhydride to a CH_2Cl_2 suspension of **1** and NEt_3 is conducted at 25 ˚C an exothermic event is observed and some CH_2Cl_2 is lost to evaporation. Assessment of the isolated reaction mixture by ^1H NMR revealed that multiple peracetylated products were present (Table 2, entry 7). The TXP and TXF regioisomers were observed in a 97:3 ratio and all four possible anomers were present in amounts similar to those observed when the reaction was performed in neat pyridine (Table 1, entries 1 and 2). It was clear that performing the reaction at 0 ˚C was crucial to obtaining the high level of regio- and stereocontrol we desired for the peracetylation of **1**. Combining the time and temperature results discussed above together (Table 2, entry 6), we performed the acetylation of **1** at 0 ˚C. The CH_2Cl_2 suspension was stirred for 30 minutes at 0 ˚C at which time no precipitate was observed, and then the reaction was quenched with H_2O at 0 ˚C. Using this optimized set of conditions, we were able to stereoselectively peracetylate α-D-xylopyranose to form **2α** along with a trace of **2β** (**2α**:**2β** = 98:2) in 99 % yield. The results for the stereoselective peracetylation of xylose detailed above compare very favorably with the solvent free method developed by Field,[10] where a high peracetylation yield of **1** was obtained but the stereochemical outcome of the reaction was not as high (**2α**:**2β** = 4:1).

The amount of control obtained over the product distribution for peracetylation of **1** through simple modifications of the reaction conditions was quite surprising. It is clear that the acetylation reaction is fast and control of the reaction temperature is crucial to limiting the number of products isolated. While it is clear that a catalytic amount of DMAP does increase the rate of the esterification reaction,[24-25] keeping the reaction temperature at 0 ˚C is necessary to prevent the faster isomerization of xylose between the pyranose and furanose regioisomers.[26] The nature of the amine base used during the peracetylation of **1** is not crucial with regards to obtaining a high yield of **2α**. When pyridine is used in place of NEt_3 (Table 2, entry 8) the TXP regioisomer was obtained in 97 % isolated yield with anomers

2α and **2β** present in a 99:1 ratio. The presence of a catalytic amount of DMAP in the reaction is crucial to obtaining a high yield of anomer **2α** as will be illustrated later.

Our new method for the formation of **2α** from **1** is a considerable improvement over published literature methods[12] with regards to choice of reagents, overall reaction time, and most importantly product regio- and stereoselectivity. We next explored the peracetylation of α-L-arabinose (**4**) with acetic anhydride using the conditions developed for the stereoselective peracetylation **1** (Scheme 4). Acetic anhydride was added to a CH_2Cl_2 suspension that contained **4** (2.0 g, 13.0 mmol), eight equivalents of NEt_3, and a catalytic amount of DMAP cooled to 0 ˚C. Unlike the peracetylation of

Scheme 4



1, the white suspension of **4** present at 0 ˚C did not dissolve within 30 minutes. Instead, the white suspension was stirred for two hours at 0 ˚C before **4** completely dissolved and became a clear yellow solution. Once all of **4** had dissolved the reaction mixture was warmed to 25 ˚C, stirred for 2 hours, subjected to an aqueous workup (see experimental section) where a yellow crystalline solid was isolated and assessed using ^{1}H NMR. The results are shown in Table 3 (entry 1). As observed in the peracetylation of **1**, the overall yield of peracetylated **4** was high. The ratio of regio- and stereoisomers was dramatically improved versus the peracetylation of **4** performed in neat pyridine but did not have the high degree of stereoselectivity observed in the formation of **2α** from **1**. ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed the yellow solid was comprised of TAP and TAF regioisomers **5** and **6** in a 95:5 ratio. For regioisomers **5** and **6** there also existed α- and β-anomers. The ratio of TAP anomers was **5α**:**5β** = 99:1 and the TAF anomers was **6α**:**6β** = 1:1. This result differs from the solvent free peracetylation of **4** disclosed by the research group of Field,[10] where the presence of furanosyl esters

6α and **6β** was not observed and the ratio of pyranosyl esters **5α** and 5β was 1:3. While the two furanosyl esters **6α**:**6β** could not be completely eliminated from the isolated reaction mixture, the minor amounts of both present along with the significantly diminished quantity of **5β** allowed for the isolation of **5α** as a white solid in 56 % yield by recrystallization of the reaction mixture using absolute ethanol (Table 3, entry 2).

Table 3. Peracetylation of α-L-arabinose (**4**) in the presence of DMAP/amine[a]

					peracetylated L-arabinose[c]					
					hemiacetal ratio[d]		anomer ratio[e]			
entry	amine	0 ˚C, t_1 (h)	25 ˚C, t_2 (h)	yield (%)[b]	5α/β	6α/β	5α	5β	6α	6β
1	NEt_3	2	2	88	95	5	99	1	50	50
2	NEt_3	2.5	2	91(56)[f]	95	5	98	2	60	40
3	NEt_3	-	2.5	98	77	23	85	15	53	47
4	pyridine	4.5	2	100	94	6	98	2	67	33

[a]Conditions: α-L-arabinose (2 g, 13 mmol, 1 equiv), DMAP (10 mol %), amine (8 equiv), and Ac_2O (7 equiv) reacted in CH_2Cl_2 (10 mL) at indicated temperatures for indicated time. [b]based on mass of all peracetylated C5 sugars present in isolated reaction mixture. [c]pyranose/furanose and anomer ratios determined by ^{1}H NMR of the reaction mixture after workup. [d]pyranose = $\alpha_p + \beta_p$; furanose = $\alpha_f + \beta_f$. [e]p = pyranose; f = furanose. [f]isolated yield of **5α**.

The melting point of the isolated white crystalline solid was determined to be 96-97 ˚C. ^{1}H NMR analysis in $CDCl_3$ confirmed that the isolated solid was indeed **5α** as a doublet at δ 6.34 ppm (J = 3.2 Hz) was observed for the equatorially disposed hydrogen attached to C1 in **5α**.[20] The published melting point for **5α** was incorrectly assigned to **5β** in the literature.[27] ^{1}H NMR analysis of filtrate residue (1.12 g) showed that it was still enriched in **5α** versus **5β**/**6α**/**6β** with an observed ratio of 81:19. Attempts to improve the yield of **5α** through recrystallization of the filtrate residue using smaller amounts of absolute ethanol met with no success.

As was observed in the peracetylation of **1** using DMAP/NEt_3, the temperature of the reaction mixture after the addition of acetic anhydride played an important role. When the reaction was not stirred at 0 ˚C, allowing all solids to completely dissolve, an exothermic event was observed and some CH_2Cl_2 was lost to evaporation. Assessment of the isolated yellow syrup by ^{1}H NMR revealed that multiple

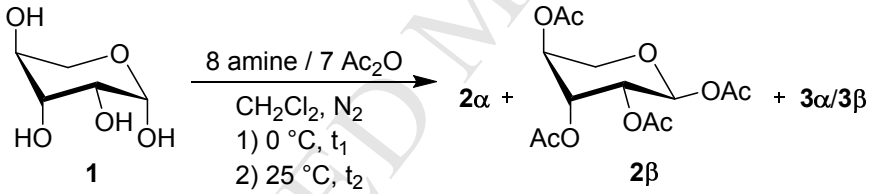
peracetylated products were present (Table 3, entry 3). The TAP and TAF regioisomers were observed in a 77:23 ratio and all four anomers were present in amounts similar to those observed when the reaction was run in neat pyridine (Table 1, entries 3 and 4). The nature of the amine base used during the peracetylation of **4** is not crucial with regards to obtaining good selectivity for the formation of **5α**. When pyridine is used in place of NEt_3 (Table 3, entry 4) the overall conversion of **4** into peracetylated products was quantitative, although a longer time stirring at 0 ˚C was required for all solids to completely dissolve. ^{1}H NMR characterization ($CDCl_3$) of the isolated reaction mixture showed the colorless crystalline solid was comprised of TAP and TAF regioisomers **5** and **6** in a 94:6 ratio, with anomer **5α** being highly enriched (93:7), very similar to what was observed when NEt_3 was employed in this reaction. This is the first reported example of the synthesis and isolation of pure **5α** in good yields. It was reported recently that heating **4** at 130 ˚C in the presence of KOAc and Ac_2O produced a mixture of **5α** and **5β** that was enriched in **5α** (5.4:1) although no ^{1}H NMR data was provided and no attempt to isolate **5α** was discussed.[28] The method disclosed here provides access to pure **5α** that is straightforward and scalable.

Peracetylation in the Absence of DMAP. The synthesis of **2α** and **5α** discussed above illustrates that temperature plays an important role in determining the regio- and stereochemical outcome of the peracetylation reactions. Our results indicate the identity of the amine base is not crucial in these peracetylation reactions. All of the reactions discussed above were performed with a catalytic amount (10 mol %) of DMAP present. It is clear that DMAP does increase the rate of esterification reactions,[24-25] but it is unknown what affect the absence of DMAP will have on the peracetylation reaction's product distribution. In an effort to further streamline the reaction conditions, both in terms of overall cost and atom economy, we were interested in exploring the product distribution of the peracetylation reaction when it was performed in the absence of DMAP.

Using the reaction conditions outlined for the stereoselective synthesis of **2α** but omitting DMAP (Scheme 5), acetic anhydride was added to a CH_2Cl_2 suspension that contained **1** (2.0 g, 13.0 mmol) and NEt_3 (8 equiv.) cooled to 0 ˚C. After two hours of stirring at 0 ˚C, the reaction mixture was still a white

suspension. The suspension was warmed to 25 ˚C with stirring and the white solid slowly dissolved. After stirring the clear yellow solution for two hours at 25 ˚C, it was subjected to an aqueous workup (see experimental section), and a white crystalline solid was isolated. The results of this reaction are shown in Table 4 (entry 1). As observed in our earlier reactions, the overall yield of peracetylated xylose was almost quantitative (95 %). The regiochemical outcome of the peracetylation reaction in the absence of DMAP again favored the formation of the pyranose isomers **2** over the furanose isomers **3** in a 94:6 ratio. The stereochemical outcome of the reaction was unexpected in both physical appearance and molecular composition. The isolated white crystalline solid consisted of tetraacetylated D-xyloses **2α** and **2β** with an anomer ratio of the 19:81 for **2α** (doublet at δ 6.21 ppm (J = 4.0, equatorial C(1)-H)) and **2β** (doublet at δ 5.71 ppm (J = 6.8, axial C(1)-H)) which was opposite the results obtained when the peracetylation reactions were performed in the presence of DMAP.

Scheme 5



While the two furanose anomers **3α**:**3β** could not be completely eliminated from the isolated reaction mixture, the minor amounts of both as well as the significantly diminished quantity of **2α** allowed for the isolation of **2β** as a white solid in 71 % yield by recrystallization of the reaction mixture using absolute 1-propanol (Table 4, entry 8). The melting point of the isolated white crystalline solid **2β** was determined to be 124-125 ˚C. The observed melting point is similar to the value published in the literature.[29] ^{1}H NMR analysis in $CDCl_3$ confirmed that the isolated solid was indeed **2β** as a doublet at δ 5.71 ppm (J = 6.8 Hz) was observed for the axially disposed hydrogen attached to C1 in **2β**.[30] ^{1}H NMR analysis of filtrate residue (4.76 g) showed that it was depleted in **2β** versus **2α**/**3α**/**3β** with an observed ratio of 12:88.

Table 4. Peracetylation of α-D-xylose (**1**) in the presence of amine[a]

					peracetylated D-xylose[c]					
					hemiacetal ratio[d]		anomer ratio[e]			
entry	amine	0 ˚C, t_1 (h)	25 ˚C, t_2 (h)	yield (%)[b]	2α/β	3α/β	2α	2β	3α	3β
1	NEt_3	2	2	95(48)[f]	94	6	19	81	25	75
2	NEt_3	2	2	88(51)[f]	94	6	14	86	29	71
3	NEt_3	4.5	2	87(40)[f]	95	5	20	80	17	83
4	NEt_3	-	2	83(49)[f]	93	7	11	89	25	75
5	NEt_3	-	2	82(44)[f]	93	7	12	88	22	78
6	NEt_3	-	2	90(48)[g]	95	5	9	91	33	67
7[h]	NEt_3	-	2	92(63)[g]	93	7	12	88	33	67
8[i]	NEt_3	-	2	93(71)[g]	92	8	9	91	20	80
9	pyridine	-	2	84	95	5	68	32	57	43

[a]conditions: α-D-xylose (2 g, 13 mmol, 1 equiv), amine (8 equiv), and Ac_2O (7 equiv) reacted in CH_2Cl_2 (10 mL) at indicated temperatures for indicated time. [b]based on mass of all peracetylated C5 sugars present in isolated reaction mixture; value in parenthesis is isolated yield of **2β**. [c]pyranose/furanose and anomer ratios determined by ^{1}H NMR of the reaction mixture after workup. [d]pyranose = $\alpha_p + \beta_p$; furanose = $\alpha_f + \beta_f$. [e]p = pyranose; f = furanose. [f]ethanol used as crystallization solvent. [g]1-propanol used as crystallization solvent. [h]conditions: α-D-xylose (5 g, 33.3 mmol, 1 equiv), amine (8 equiv), and Ac_2O (7 equiv) reacted in CH_2Cl_2 (25 mL) at indicated temperatures for indicated time. [i]conditions: α-D-xylose (10 g, 66.6 mmol, 1 equiv), amine (8 equiv), and Ac_2O (7 equiv) reacted in CH_2Cl_2 (50 mL) at indicated temperatures for indicated time.

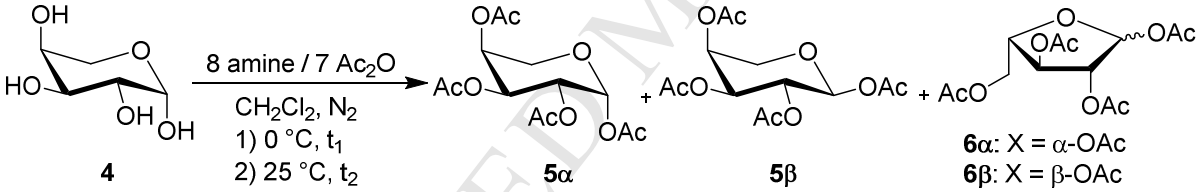
It was determined that the peracetylation of **1** in the absence of DMAP does not have to be cooled to 0 °C and the reaction can be performed at 25 °C without an adverse effect on the isolated yield of **2β** (Table 4, entries 4 through 8). This makes the synthesis of **2β** from **1** in the presence of NEt_3 and acetic anhydride operationally straightforward and simple.

Unlike our earlier results for the stereoselective peracetylation of **2α**, where the nature of the amine base used was not crucial to obtaining high stereoselectivity, a change in the amine used for the peracetylation of **1** in the absence of DMAP led to very different results. When pyridine is used in place of NEt_3 (Table 4, entry 9), the overall conversion of **1** to peracetylated products was high but multiple products were observed. ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed the colorless oil was comprised of regioisomers **2** and **3** in a ratio of 95:5. For both **2** and **3** there also existed α- and β-anomers. The ratio of TXP anomers was **2α**:**2β** = 68:32 and the TXF anomers was **3α**:**3β** =

57:43. These isomer ratios are identical to those obtained when **1** was peracetylated in neat pyridine (Table 1, entry 2) and are not desirable. It is clear that to obtain high isolated yields of **2β** the choice of amine base is important. The success of this reaction using NEt_3 creates an ideal situation where the outcome of the reaction can be predetermined by the presence or absence of DMAP. This shows the potential for using this reaction early in a biorefinery chemical process, forming two products that could be used in different applications; **2α** for continued processing into fuels and materials,[31] and **2β** for surfactants and medical applications.[32]

Our new method for the formation of **2β** from **1** is an improvement over published literature methods[29] with regards to choice of reagents and overall reaction time. We next explored the peracetylation of α-L-arabinose (**4**) with acetic anhydride using the conditions developed for the peracetylation in the absence of DMAP (Scheme 6). Acetic anhydride was added to a CH_2Cl_2 suspension

Scheme 6



that contained **4** (2.0 g, 13.0 mmol) and eight equivalents of NEt_3 cooled to 0 ˚C. Unlike the peracetylation of **4** in the presence of DMAP, the white suspension of **4** did not dissolve even after 4 hours at 0 ˚C. The white suspension was warmed to 25 ˚C, stirred for 2 hours, the resulting clear yellow solution was subjected to an aqueous workup (see experimental section), and a yellow glass was isolated. The results are shown in Table 5 (entry 1). As observed in previous peracetylation reactions, the overall yield of peracetylated **4** was high. The regiochemical outcome of the peracetylation reaction of **4** in the absence of DMAP favored the formation of the pyranosyl ester **5** over the furanozyl ester **6**. ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed the yellow glass was comprised of TAP and TAF regioisomers **5** and **6** in a 67:33 ratio. The ratio of TAP anomers was **5α**:**5β** = 9:91 and the TAF

anomers was **6α:6β** = 44:56. Attempts to isolate **5β** from the reaction mixture via crystallization were not successful.

Table 5. Peracetylation of α-L-arabinose (**4**) in the presence of amine[a]

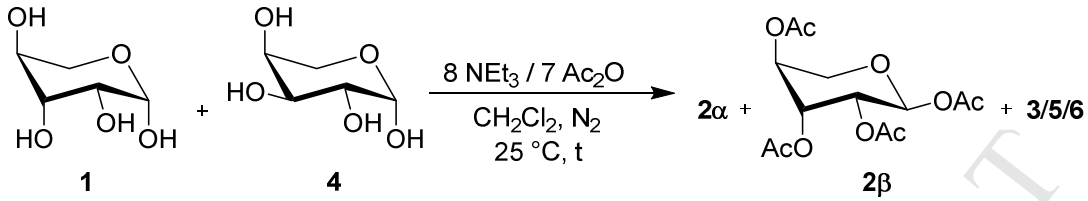
					peracetylated L-arabinose[c]					
					hemiacetal ratio[d]		anomer ratio[e]			
entry	amine	0 ˚C, t_1 (h)	25 ˚C, t_2 (h)	yield (%)[b]	5α/β	6α/β	5α	5β	6α	6β
1	NEt_3	4	2	78	67	33	9	91	44	56
2	NEt_3	4	2	82	66	34	11	89	46	54
3	NEt_3	-	4	88	70	30	7	93	43	57

[a]Conditions: α-L-arabinose (2 g, 13 mmol, 1 equiv), amine (8 equiv), and Ac_2O (7 equiv) reacted in CH_2Cl_2 (10 mL) at indicated temperatures for indicated time. [b]based on mass of all peracetylated C5 sugars present in isolated reaction mixture. [c]pyranose/furanose and anomer ratios determined by ^1H NMR of the reaction mixture after workup. [d]pyranose = $\alpha_p + \beta_p$; furanose = $\alpha_f + \beta_f$. [e]p = pyranose; f = furanose.

Peracetylation as a Separation Method. As mentioned above, we are pursuing the use of D-xylose and L-arabinose as starting materials for synthesis of a variety of industrially important chemicals traditionally obtained from petroleum. We have disclosed a boronic acid mediated isolation protocol which delivers D-xylose and L-arabinose in a 83:17 ratio of the two pentoses.[15] This process does provide a mixture of pure monosaccharides but separation and isolation of each pentose is required for subsequent synthetic transformations to be accomplished. Based on our ability to isolate pure **2β** and **5α** using our peracetylation methodologies followed by selective crystallization, we felt this could be a route to isolate pure D-xylose and L-arabinose, albeit as their acetylated derivatives (Scheme 7 and 8).

Using the reaction conditions outlined for the stereoselective synthesis of **2β**, acetic anhydride was added to a CH_2Cl_2 suspension that contained a 85:15 mixture of **1** and **4** (2.0 g, 13.0 mmol) and NEt_3 (8 equiv.) cooled to 0 ˚C (Scheme 7). After two hours of stirring at 25 ˚C, the reaction mixture was a clear yellow solution. The solution was subjected to an aqueous workup (see experimental section), and a white crystalline solid was isolated. The results of this reaction are shown in Table 6 (entry 1).

Scheme 7



The overall yield of peracetylated pentoses was high (76 %). The ratio of peracetylated D-xylose compared to peracetylated L-arabinose (81:19) was very close to the ratio of the two starting pentoses. The ratio of **2β** versus **2α/3/5/6** in the reaction residue was determined to be 66:34. Recystallization of the reaction mixture using ethanol allowed for the isolation of the D-xylose derivative **2β** in 45 % yield. Melting point and ^{1}H NMR analysis verified the identity of the crystalline white solid as **2β**. ^{1}H NMR analysis of crystallization filtrate showed that it was depleted in **2β** versus **2α/3/5/6**with an observed ratio of 18:82. Doubling the peracetylation reaction time to 4 hours at 25 °C, led to an increase in the overall yield of peracetylated products as shown in entry 2 of Table 6. The ratio of peracetylated D-xylose compared to peracetylated L-arabinose (81:19) was identical to the previous reaction with only a minor increase in the isolated yield of **2β** obtained. The pentose mixtures used in entries 2 and 3 of Table 6 were obtained from DDG derived hydrolyzate.[15]

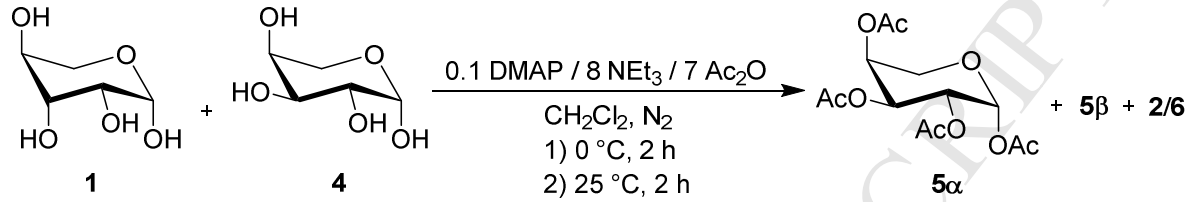
Table 6. Isolation of **2β** from a mixture of pentoses **1**/**4** using NEt_3/Ac_2O[a]

				peracetylated pentoses[e]		
				acetylated C5 ratio	rxn mixture	filtrate residue
entry	**ratio 1:4**	**25 ˚C, t (h)**	**yield (%)[d]**	**2/3 : 5/6**	**2β : 2α/3/5/6**	**2β : 2α/3/5/6**
1	85:15[b]	2	76(45)[f]	81:19	66:34	18:82
2	83:17[c]	4	97(47)[f]	81:19	68:32	24:76
3	83:17[c]	2	87(40)[f]	78:22	63:37	20:80

[a]Conditions: pentoses **1**/**4** (2 g, 13 mmol, 1 equiv), amine (8 equiv), and Ac_2O (7 equiv) reacted in CH_2Cl_2 (10 mL) at 25 ˚C for indicated time. [b]mixture (m/m) made using commercially purchased D-xylose/L-arabinose, pentose ratio determined using ^{1}H NMR. [c]isolated sugar mixture from ref 15, pentose ratio determined using ^{1}H NMR. [d]based on mass of all peracetylated C5 sugars present in isolated reaction mixture; value in parenthesis is isolated yield of **2β**. [e]pentose, pyranose/furanose and anomer ratios determined by ^{1}H NMR of the reaction mixture after workup. [f]ethanol used as crystallization solvent.

Isolation of pure L-arabinose derivative **5α** can be achieved starting with an arabinose enriched (4.4:1) mixture of **4** and **1** using a catalytic amount of DMAP in the presence of NEt_3 at 0 °C (Scheme 8). Acetic anhydride was added to a CH_2Cl_2 suspension that contained a mixture of **4** and **1 (**4.4:1)

Scheme 8



(2.0 g, 13.0 mmol), eight equivalents of NEt_3, and a catalytic amount of DMAP cooled to 0 ˚C. The white suspension was stirred for two hours at 0 ˚C before all solids completely dissolved and became a clear yellow solution. Once all of the solids had dissolved the reaction mixture was warmed to 25 ˚C, stirred for 2 hours, subjected to an aqueous workup (see experimental section), and a yellow crystalline solid was isolated. The results are shown in Table 7. The overall yield of peracetylated pentoses was almost quantitative (98 %). The ratio of peracetylated L-arabinose compared to peracetylated D-xylose (81:19)

Table 7. Isolation of **5α** from a mixture of pentoses **4**/**1** using DMAP/NEt_3/Ac_2O[a]

			peracetylated pentoses[d]		
			acetylated C5 ratio	rxn mixture	filtrate residue
entry	**ratio 4:1[b]**	**yield (%)[c]**	**5/6 : 2**	**5α : 2/5/6**	**5α : 2/5/6**
1	4.4:1	98(42)[e]	81:19	74:26	53:47
2	4.4:1	99(40)[e]	81:19	75:25	55:45

[a]Conditions: pentoses **4**/**1** (2 g, 13 mmol, 1 equiv), DMAP (10 mol %), amine (8 equiv), and Ac_2O (7 equiv) reacted in CH_2Cl_2 (10 mL) at 0 ˚C for 2 hours and at 25 ˚C for 2 hours. [b]mixture (m/m) made using commercially purchased D-xylose/L-arabinose, pentose ratio determined using ^{1}H NMR. [c]based on mass of all peracetylated C5 sugars present in isolated reaction mixture; value in parenthesis is isolated yield of **5α**. [d]pentose, pyranose/furanose and anomer ratios determined by ^{1}H NMR of the reaction mixture after workup. [e]1-propanol used as crystallization solvent.

was very close to the ratio of the two starting pentoses. The ratio of **5α** versus **2/5/6** in the reaction residue was determined to be 74:26. Recystallization of the reaction mixture using 1-propanol allowed for the isolation of the L-arabinose derivative **5α** in 42 % yield. Melting point and ^{1}H NMR analysis

verified the identity of the crystalline white solid as **5α**. ^{1}H NMR analysis of crystallization filtrate showed that it was depleted in **2β** versus **2/5/6**with an observed ratio of 53:47.

Peracetylation is a very common protection strategy that is widely implemented in carbohydrate synthesis. In summary, we developed a straightforward, time-conservative that allows for stereo-selective peracetylation of the C5 sugars, D-xylose and L-arabinose, to form either α or β pyranosyl esters in high yields. The stereoselective peracetylation reactions were used to separate mixtures of D-xylose and L-arabinose obtained from hydrolyzate of distillers dried grains (DDG) to provide pure pentoses as their peracetylated derivatives in good yields.

Experimental Section

General Experimental Details. All reactions were carried out in oven-dried glassware under N_2 unless otherwise specified. N_2 was purified by passage through columns containing activated molecular sieves and Q-5 oxygen scavenger. Dichloromethane was purified by passage through columns of activated 4 Å molecular sieves. All reagents were purchased from commercial sources and used without further purification unless noted. ^{1}H and ^{13}C NMR spectra were recorded in capped tubes on Varian 400 and 500 spectrometers at ambient probe temperature unless otherwise indicated. ^{1}H and ^{13}C chemical shifts are reported versus $SiMe_4$ and were determined by reference to the residual ^{1}H and ^{13}C solvent peaks. Chemical shift, regiochemical and stereochemical assignments for the starting D-xylose and L-arabinose were made by preparing samples of each in DMSO-d_6 and obtaining NMR spectra for both solutions. For D-xylose, ^{1}H, ^{13}C[33], and multidimensional NMR (^{1}H-^{1}H COSY and ^{1}H-^{13}C one bond correlation) were obtained and comparison to literature chemical shift values[34] allowed for the assignment of hydroxyl protons, the C1 (anomeric) proton and only α-D-xylose was observed. For L-arabinose in DMSO-d_6, very little information exists in the literature except for hydroxyl proton chemical shift values[35] so ^{1}H, ^{13}C[33], and multidimensional NMR (^{1}H-^{1}H COSY and ^{1}H-^{13}C one bond correlation) were obtained to assign the anomeric proton and determine its stereochemcial orientation. Interpretation of the data from these NMR experiments allowed for the assignment of the starting L-arabinose as the α anomer.

α-D-xylopyranose (1): ^{1}H NMR (DMSO-d_6): δ 6.12 (d, *J* = 4.8, 1H, 1-O*H*), 4.84 (t, *J* = 8.4, 1H, H-1), 4.80 (d, *J* = 5.2, 1H, 4-O*H*), 4.68 (d, *J* = 4.4, 1H, 3-O*H*), 4.45 (d, *J* = 6.4, 1H, 2-O*H*), 3.47 (m, 1H, H-5), 3.35 (m, 2H, H-5', H-3), 3.22 (m, 1H, H-4), 3.11 (m, 1H, H-2). $^{13}C^{33}$ NMR (DMSO-d_6): δ 92.5 (C1), 73.2 (C3), 72.4 (C2), 70.2 (C4), 61.6 (C5).

α-L-arabinopyranose (4): ^{1}H NMR (DMSO-d_6): δ 6.00 (d, *J* = 5.6, 1H, 1-O*H*), 4.85 (dd, *J* = 5.2, 2.4, 1H, H-1), 4.49 (d, *J* = 5.2, 1H, 3-O*H*), 4.39 (s, 1H, 4-O*H*), 4.38 (d, *J* = 2.4, 1H, 2-O*H*), 3.67 (m, 2H, H-4, H-5), 3.59 (m, 1H, H-3), 3.46 (m, 1H, H-2), 3.37 (dd, *J* = 12.4, 4.8, 1H, H-5'). $^{13}C^{33}$ NMR (DMSO-d_6): δ 92.7 (C1), 69.5 (C3), 69.3 (C2), 67.5 (C4), 62.6 (C5).

Tetra-*O*-acetyl-α-D-xylopyranose (2α): ^{1}H NMR ($CDCl_3$): δ 6.21 (d, *J* = 4.0, H-1 of 2α), 5.42 (t, *J* = 10.0, H-3 of 2α), 4.98 (m, H-2, H-4), 3.89 (dd, *J* = 10.8, 6.0 H-5 of 2α), 3.66 (t, *J* = 10.8, H-5' of 2α), 2.14 (s, 3H, OAc C*H*$_3$), 2.02 (s, 6H, OAc C*H*$_3$), 1.99 (s, 3H, OAc C*H*$_3$).

Tetra-*O*-acetyl-β-D-xylopyranose (2β): ^{1}H NMR ($CDCl_3$): δ 5.71 (d, *J* = 6.8, 1H, H-1), 5.20 (t, *J* = 8.0, 1H, H-3), 5.01 (m, 2H, H-2, H-4), 4.14 (dd, *J* = 12.0, 4.8, 1H, H-5), 3.52 (dd, *J* = 12.0, 8.8, 1H, H-5'), 2.10 (s, 3H, OAc C*H*$_3$), 2.06 (s, 3H, OAc C*H*$_3$), 2.05 (s, 6H, OAc C*H*$_3$).

Tetra-*O*-acetyl-α-L-arabinopyranose (5α): ^{1}H NMR ($CDCl_3$): δ 6.34 (d, *J* = 3.2, 1H, H-1), 5.35 (m, 3H, H-2), 4.06 (d, *J* = 13.2 1H, H-4), 3.82 (dd, *J* = 13.2, 2.0, 1H, H-3), 2.15 (s, 6H, OAc C*H*$_3$), 2.02 (s, 6H, OAc C*H*$_3$).

Tetra-*O*-acetyl-β-L-arabinopyranose (5β): ^{1}H NMR ($CDCl_3$): δ 5.60 (d, *J* = 7.2, 1H, H-1), 5.23 (m, 3H, H-2, H-4), 5.05 (dd, *J* = 8.8, 3.6, 1H, H-3), 3.96 (dd, *J* = 13.2, 4.0, 1H, H-5).

Peracetylation of xylose in neat pyridine **(Table 1, entry 1)**.[16] α-D-xylose (**1**) (8.00 g, 53.3 mmol) was added to a flask under N_2. Pyridine (34.4 mL, 426.4 mmol) was added to the flask and the white suspension was stirred at 25 ˚C. Acetic anhydride (40.3 mL, 426.4 mmol) was added slowly to the flask. The suspension was stirred at 25 ˚C overnight. The solution turned clear after 15 minutes at 25 ˚C. After

stirring overnight, the solution flask was quenched with chilled DI water (100 mL). The solution was transferred to a 500 mL separatory funnel, washed with CH_2Cl_2 (3 x 100 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (3 x 100 mL), chilled DI water (4 x 100 mL), saturated $NaHCO_3$ (2 x 100 mL), and chilled DI water (2 x 100 mL). The CH_2Cl_2 layer was dried over Na_2SO_4, filtered through celite, and the solvent was removed under vacuum to yield a yellow oil (20.14 g, 100%). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained both tetraacetylated D-xylopyranoses **2α/β** and tetraacetylated D-xylofuranoses **3α/β** in a ratio of 94:6. The ratio of stereoisomers/anomers was **2α**:**2β** = 6:4 and **3α**:**3β** = 1:1. ^{1}H NMR ($CDCl_3$): key resonances of four products δ: 6.38 (d, *J* = 4.4, H-1 of 3α), 6.21 (d, *J* = 4.0, H-1 of 2α), 6.07 (s, H-1 of 3β), 5.67 (d, *J* = 6.8, H-1 of 2β), 5.42 (t, *J* = 10.0, H-3 of 2α), 5.16 (t, *J* = 8.0, H-3 of 2β), 4.98 (m, H-2 of 2α/2β, H-4 of 2α/2β), 4.10 (dd, *J* = 12.0, 4.8, H-5 of 2β), 3.89 (dd, *J* = 10.8, 6.0, H-5 of 2α), 3.66 (t, *J* = 10.8, H-5' of 2α), 3.48 (dd, *J* = 12.0, 8.8, H-5' of 2β).

Peracetylation of arabinose in neat pyridine **(Table 1, entry 3).**[20] α-L-arabinose (**4**) (4.50 g, 30.0 mmol) was added to a flask under N_2. Pyridine (19.3 mL, 240.0 mmol) was added to the flask and the white suspension was stirred at 25 ˚C. Acetic anhydride (22.6 mL, 240.0 mmol) was added slowly to the flask. The suspension was stirred at 25 ˚C overnight. After stirring overnight, the solution flask was quenched with chilled DI water (75 mL). The solution was transferred to a 500 mL separatory funnel, washed with CH_2Cl_2 (3 x 75 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (3 x 75 mL), chilled DI water (2 x 75 mL), saturated $NaHCO_3$ (1 x 75 mL), and chilled DI water (1 x 75 mL). The CH_2Cl_2 layer was dried over Na_2SO_4, filtered through celite, and the solvent was removed under vacuum to yield a yellow oil (11.11 g, 100%). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained both tetraacetylated L-arabinopyranoses **5α/β** and tetraacetylated L-arabinofuranoses **6α/β** in a ratio of 73:27. The ratio of stereoisomers/anomers was **5α**:**5β** = 6:4 and **6α**:**6β** = 4:6. ^{1}H NMR ($CDCl_3$): key resonances of four products δ 6.38 (m, H-1 of 6α), 6.34 (d, *J* = 3.2, H-1 of 5α), 6.19 (s, H-1 of 6β), 5.65 (d, *J* = 7.2,

H-1 of 5β), 5.36 (m, H-2 of 5α), 5.32 (m, H-4 of 5β), 5.30 (m, H-2 of 5β), 5.11 (dd, *J* = 8.8, 3.6, H-3 of 5β), 4.37 (m, H-4 of 5α), 4.22 (m, H-3 of 5α), 3.78 (m, H-5 of 5α and 5β).

DMAP/NEt_3 mediated peracetylation of xylose **(Table 2, entry 1)**. α-D-xylose (**1**) (2.03 g, 13.32 mmol) and DMAP (0.17 g, 1.33 mmol) were added to a flask under N_2. CH_2Cl_2 (10 mL) and NEt_3 (15 mL, 106.56 mmol) were added to the flask and the white suspension was stirred at 25 ˚C. The flask was cooled to 0 ˚C and stirred for 10 minutes. Acetic anhydride (9 mL, 93.25 mmol) was added dropwise to the flask. The white suspension was stirred at 0 ˚C for 1 hour. After 1 hour, the clear, yellow solution was removed from the ice bath and warmed to 25 ˚C. The solution was stirred at 25 ˚C for 4 hours. After 4 hours, the solution flask was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes and the bi-phasic, yellow solution was stirred for 12 hours. The solution was transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a yellow glass (4.20 g, 99%). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained **2α** as the major product (98%) and a trace amount of **2β** (2%).

DMAP/NEt_3 mediated peracetylation of xylose **(Table 2, entry 3)**. α-D-xylose (**1**) (2.00 g, 13.32 mmol) and DMAP (0.17 g, 1.33 mmol) were added to a flask under N_2. CH_2Cl_2 (10 mL) and NEt_3 (15 mL, 106.56 mmol) were added to the flask and the white suspension was stirred at 25 ˚C. The flask was cooled to 0 ˚C and stirred for 10 minutes. Acetic anhydride (9 mL, 93.25 mmol) was added dropwise to the flask. The white suspension was stirred at 0 ˚C for 30 minutes. After 30 minutes, the clear, yellow solution was removed from the ice bath and warmed to 25 ˚C. The solution was stirred at 25 ˚C for 2 hours. After 2 hours, the solution flask was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes. The bi-phasic, yellow solution was then transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI

water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a yellow glass (3.98 g, 94%). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained **2α** as the major product (98%) and a trace amount of **2β** (2%).

DMAP/NEt$_3$ mediated peracetylation of xylose **(Table 2, entry 4)**. α-D-xylose (**1**) (2.00 g, 13.32 mmol) and DMAP (0.17 g, 1.33 mmol) were added to a flask under N_2. CH_2Cl_2 (10 mL) and NEt_3 (15 mL, 106.56 mmol) were added to the flask and the white suspension was stirred at 25 ˚C. The flask was cooled to 0 ˚C and stirred for 10 minutes. Acetic anhydride (9 mL, 93.25 mmol) was added dropwise to the flask. The white suspension was stirred at 0 ˚C for 30 minutes. After 30 minutes, the clear, yellow solution was removed from the ice bath and warmed to 25 ˚C. The solution was stirred at 25 ˚C for 30 minutes. After 30 minutes, the solution flask was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes. The bi-phasic, yellow solution was then transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a yellow glass (4.26 g, 100%). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained **2α** as the major product (98%) and a trace amount of **2β** (2%).

DMAP/NEt$_3$ mediated peracetylation of xylose **(Table 2, entry 6)**. α-D-xylose (**1**) (2.00 g, 13.32 mmol) and DMAP (0.17 g, 1.33 mmol) were added to a flask under N_2. CH_2Cl_2 (10 mL) and NEt_3 (15 mL, 106.56 mmol) were added to the flask and the white suspension was stirred at 25 ˚C. The flask was cooled to 0 ˚C and stirred for 10 minutes. Acetic anhydride (9 mL, 93.25 mmol) was added dropwise to the flask. The white suspension was stirred at 0 ˚C for 30 minutes. After 30 minutes, chilled DI water (20 mL) was added to the clear, yellow solution and the resulting biphasic solution was stirred at 0 ˚C for 20 minutes. The solution was transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL)

and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a yellow glass (4.23 g, 99%). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained **2α** as the major product (98%) and a trace amount of **2β** (2%).

DMAP/NEt_3 mediated peracetylation of xylose **(Table 2, entry 7)**. α-D-xylose (**1**) (2.03 g, 13.32 mmol) and DMAP (0.17 g, 1.33 mmol) were added to a flask under N_2. CH_2Cl_2 (10 mL) and NEt_3 (15 mL, 106.56 mmol) were added to the flask and the white suspension was stirred at 25 ˚C. Acetic anhydride (9 mL, 93.25 mmol) was added dropwise to the flask, where the white suspension warmed to the touch. The white suspension was stirred at 25 ˚C for 2 hours and 30 minutes. After 2 hours and 30 minutes, the solution flask was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes and the bi-phasic, yellow solution was transferred to a 250 mL separatory funnel. The solution was washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a yellow syrup (3.67 g, 87%). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained both **2α/β** and **3α/β** in a ratio of 93:7. The ratio of stereoisomers/anomers was **2α**:**2β** = 72:28 and **3α**:**3β** = 1:1.

DMAP/pyridine mediated peracetylation of xylose **(Table 2, entry 8)**. α-D-xylose (**1**) (2.00 g, 13.32 mmol) and DMAP (0.17 g, 1.33 mmol) were added to a flask under N_2. CH_2Cl_2 (10 mL) and Pyridine (9 mL, 106.56 mmol) were added to the flask and the white suspension was stirred at 25 ˚C. The flask was cooled to 0 ˚C and stirred for 10 minutes. Acetic anhydride (9 mL, 93.25 mmol) was added dropwise to the flask. The white suspension was stirred at 0 ˚C for 1 hour. After 1 hour, the clear, colorless solution

was removed from the ice bath and warmed to 25 ˚C. The solution was stirred at 25 ˚C for 2 hours. After 2 hours, the solution flask was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes and the bi-phasic, colorless solution was stirred for 12 hours. The solution was transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a colorless syrup (4.12 g, 97%). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained **2α** as the major product (99%) and a trace of **2β** (1%).

DMAP/NEt$_3$ mediated peracetylation of xylose **(Table 2, entry 9)**. α-D-xylose (**1**) (10.0 g, 66.6 mmol) and DMAP (0.817 g, 6.66 mmol) were added to a flask under N_2. CH_2Cl_2 (50 mL) and NEt_3 (74 mL, 532.8 mmol) were added to the flask and the white suspension was stirred at 25 ˚C. The flask was cooled to 0 ˚C and stirred for 10 minutes. Acetic anhydride (44 mL, 466.2 mmol) was added in 15 mL portions to the flask. The Ac_2O portions were added in 10 minute intervals to prevent excessive heating of the mixture. The white suspension was stirred at 0 ˚C for 1 hour. After 1 hour, the clear, yellow-orange solution was removed from the ice bath and warmed to 25 ˚C. The solution was stirred at 25 ˚C for 19 hours. After 19 hours, the solution flask was placed in an ice bath and quenched with chilled DI water (100 mL). The ice bath was removed after 20 minutes and the bi-phasic, yellow-orange solution was stirred for 12 hours. The reaction mixture was transferred to a 1 L separatory funnel and was washed with CH_2Cl_2 (3 x 100 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 100 mL), chilled DI water (3 x 100 mL), saturated $NaHCO_3$ (3 x 100 mL), and chilled DI water (2 x 100 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield an orange glass (23.56 g, 100%). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained **2α** as the major product (96%) and a trace amount of **2β** (4%).

DMAP/NEt_3 mediated peracetylation of arabinose **(Table 3, entry 1)**. α-L-arabinose (**4**) (2.00 g, 13.32 mmol) and DMAP (0.17 g, 1.33 mmol) were added to a flask under N_2. CH_2Cl_2 (10 mL) and NEt_3 (15 mL, 106.56 mmol) were added to the flask and the white suspension was stirred at 25 ˚C. The flask was cooled to 0 ˚C and stirred for 10 minutes. Acetic anhydride (9 mL, 93.25 mmol) was added dropwise to the flask. The white suspension was stirred at 0 ˚C for 2 hours. After 2 hours, the clear, yellow solution was removed from the ice bath and warmed to 25 ˚C. The solution was stirred at 25 ˚C for 2 hours. After 2 hours, the solution flask was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes and the bi-phasic, yellow solution was transferred to a 250 mL separatory funnel. The solution was washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a yellow crystal (3.75 g, 88%). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained both **5α/β** and **6α/β** in a ratio of 95:5. The ratio of stereoisomers/anomers was **5α**:**5β** = 99:1 and **6α**:**6β** = 1:1.

DMAP/NEt_3 mediated peracetylation of arabinose **(Table 3, entry 2)**. α-L-arabinose (**4**) (2.00 g, 13.32 mmol) and DMAP (0.17 g, 1.33 mmol) were added to a flask under N_2. CH_2Cl_2 (10 mL) and NEt_3 (15 mL, 106.56 mmol) were added to the flask and the white suspension was stirred at 25 ˚C. The flask was cooled to 0 ˚C and stirred for 10 minutes. Acetic anhydride (9 mL, 93.25 mmol) was added dropwise to the flask. The white suspension was stirred at 0 ˚C for 2 hours and 30 minutes. After 2 hours and 30 minutes, the clear, yellow solution was removed from the ice bath and warmed to 25 ˚C. The solution was stirred at 25 ˚C for 2 hours. After 2 hours, the solution flask was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes and the bi-phasic, yellow solution was transferred to a 250 mL separatory funnel. The solution was washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed

with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a yellow crystal (3.84 g, 91%). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained both **5α/β** and **6α/β** in a ratio of 95:5 while the ratio of **5α** to **5β/6α/6β** was 93:7. The ratio of stereoisomers/anomers was **5α**:**5β** = 98:2 and **6α**:**6β** = 3:2. Absolute EtOH (60 ml) was used to transfer the crystals to a 100 mL beaker with stir bar. The mixture was heated and stirred to dissolve the crystals. The solution volume was reduced to 30 mL with heating. The beaker was then removed from the heat and allowed to cool to 25 ˚C. The solution was agitated which yielded white crystals. The crystals were collected by filtration with a Buchner funnel and dried to afford a white, crystalline solid (2.38 g, 56%), mp 96-97 ˚C. The solid was characterized by ^{1}H NMR ($CDCl_3$) and identified as **5α.** The solvent from the filtrate was removed under vacuum to yield 1.12 g of an orange oil. ^{1}H NMR characterization of the filtrate residue in $CDCl_3$ showed the ratio of **5α/β** and **6α/β** was 85:15 while the ratio of **5α** to **5β/6α/6β** had changed to 81:19. The ratio of stereoisomers/anomers was **5α**:**5β** = 95:5 and **6α**:**6β** = 63:37.

DMAP/NEt_3 mediated peracetylation of arabinose **(Table 3, entry 3)**. α-L-arabinose (**4**) (2.00 g, 13.32 mmol) and DMAP (0.17 g, 1.33 mmol) were added to a flask under N_2. CH_2Cl_2 (10 mL) and NEt_3 (15 mL, 106.56 mmol) were added to the flask. Acetic anhydride (9 mL, 93.25 mmol) was added dropwise to the flask, where the white suspension warmed to the touch. The solution was stirred at 25 ˚C for 2 hours and 30 minutes. After 2 hours and 30 minutes, the solution flask was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes and the bi-phasic, yellow solution was allowed to stir for 12 hours. The solution was transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a yellow syrup (4.17

g, 98%). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained both **5α/β** and **6α/β** in a ratio of 77:23. The ratio of stereoisomers/anomers was **5α**:**5β** = 85:15 and **6α**:**6β** = 53:47.

DMAP/pyridine mediated peracetylation of arabinose **(Table 3, entry 4)**. α-L-arabinose (**4**) (2.00 g, 13.32 mmol) and DMAP (0.17 g, 1.33 mmol) were added to a flask under N_2. CH_2Cl_2 (10 mL) and pyridine (9 mL, 106.56 mmol) were added to the flask and the suspension was stirred at 25 ˚C. The white suspension was then stirred at 0 ˚C for 10 minutes. Acetic anhydride (9 mL, 93.25 mmol) was added dropwise to the flask. The mixture was stirred at 0 ˚C for 4 hours and 30 minutes. After 4 hours and 30 minutes, the clear, colorless solution was stirred at room temperature for 2 hours. After 2 hours, the reaction flask was placed in an ice bath and the solution was quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes and the bi-phasic, colorless solution was allowed to stir for 12 hours. The solution was transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield clear crystals (4.27 g, 100%). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained both **5α/β** and **6α/β** in a ratio of 94:6. The ratio of stereoisomers/anomers was **5α**:**5β** = 98:2 and **6α**:**6β** = 2:1.

NEt_3 mediated peracetylation of xylose **(Table 4, entry 1)**. α-D-xylose (**1**) (2.00 g, 13.32 mmol) was added to a 100 mL round bottom flask under N_2. CH_2Cl_2 (10 mL) and NEt_3 (15 mL, 106.56 mmol) were added to the flask and the white suspension was stirred at 25 ˚C. The flask was cooled to 0 ˚C and stirred for 10 minutes. Ac_2O (9 mL, 93.25 mmol) was added dropwise to the flask. The white suspension was stirred at 0 ˚C for 2 hours. After 2 hours, the solution was still a white suspension and the flask was removed from the ice bath and warmed to 25 ˚C. The reaction mixture was stirred at 25 ˚C for 2 hours. After 2 hours, the clear yellow solution was placed in an ice bath and quenched with chilled DI water (20

mL). The ice bath was removed after 20 minutes and the bi-phasic, yellow suspension was stirred for 12 hours. The solution was transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a white crystalline solid (4.03 g). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained both **2α/β** and **3α/β** in a ratio of 94:6 while the ratio of **2β** to **2α/3α/3β** was 76:24. The ratio of stereoisomers/anomers was **2α**:**2β** = 19:81 and **3α**:**3β** = 25:75. Absolute EtOH (60 mL) was then added to the crystals. The crystals dissolved in EtOH when the solution was heated. The solution volume was reduced to 30 mL with heating. The flask was then removed from heat and allowed to cool to 25 ˚C. The solution was agitated which yielded white crystals. The crystals were collected by filtration with a Buchner funnel and dried to afford a white, crystalline solid (2.05g, 48%), mp 123-124 ˚C (lit.[29] 125-128 ˚C). The solid was characterized by ^{1}H NMR ($CDCl_3$) and identified as **2β**.

NEt_3 mediated peracetylation of xylose **(Table 4, entry 3)**. α-D-xylose (**1**) (2.00 g, 13.32 mmol) was added to a 100 mL round bottom flask under N_2. CH_2Cl_2 (10 mL) and NEt_3 (15 mL, 106.56 mmol) were added to the flask and the white suspension was stirred at 25 ˚C. The flask was cooled to 0 ˚C and stirred for 10 minutes. Ac_2O (9 mL, 93.25 mmol) was added dropwise to the flask. The white suspension was stirred at 0 ˚C for 4.5 hours. After 4.5 hours, the solution was still a white suspension and the flask was removed from the ice bath and warmed to 25 ˚C. The reaction mixture was stirred at 25 ˚C for 2 hours. After 2 hours, the clear yellow solution was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes and the bi-phasic, yellow suspension was stirred for 12 hours. The solution was transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI

water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a white crystalline solid (3.86 g). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained both **2α/β** and **3α/β** in a ratio of 95:5 while the ratio of **2β** to **2α/3α/3β** was 76:24. The ratio of stereoisomers/anomers was **2α**:**2β** = 20:80 and **3α**:**3β** = 17:83. Absolute EtOH (60 mL) was then added to the crystals. The crystals dissolved in EtOH when the solution was heated. The solution volume was reduced to 30 mL with heating. The flask was then removed from heat and allowed to cool to 25 ˚C. The solution was agitated which yielded white crystals. The crystals were collected by filtration with a Buchner funnel and dried to afford a white, crystalline solid (1.68 g, 40%), mp 124 ˚C (lit.[29] 125-128 ˚C).

NEt_3 mediated peracetylation of xylose **(Table 4, entry 4)**. α-D-xylose (**1**) (2.00 g, 13.32 mmol) was added to a 100 mL round bottom flask under N_2. CH_2Cl_2 (10 mL), NEt_3 (15 mL, 106.56 mmol) and Ac_2O (9 mL, 93.25 mmol) were added to the flask, where the white suspension warmed to the touch. The white suspension was stirred at 25 ˚C for 2 hours. After 2 hours, the clear yellow solution was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes. The solution was transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a white crystalline solid (3.5 g). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained both **2α/β** and **3α/β** in a ratio of 93:7 while the ratio of **2β** to **2α/3α/3β** was 88:12. The ratio of stereoisomers/anomers was **2α**:**2β** = 11:89 and **3α**:**3β** = 25:75. Absolute EtOH (60 mL) was then added to the crystals. The crystals dissolved in EtOH when the solution was heated. The solution volume was reduced to 30 mL with heating. The flask was then removed from heat and allowed to cool to 25 ˚C. The solution was agitated which yielded white crystals. The crystals were collected by filtration and dried to afford a white, crystalline solid (2.09 g, 49%), mp 123-124 ˚C

(lit.[29] 125-128 ˚C). The solid was characterized by ^{1}H NMR ($CDCl_3$) and identified as **2β**. The solvent from the filtrate was removed under vacuum to yield 1.41 g of a yellow oil. ^{1}H NMR characterization of the filtrate residue in $CDCl_3$ showed the ratio of **2α/β** and **3α/β** was 72:28 while the ratio of **2β** to **2α/3α/3β** had changed to 30:70. The ratio of stereoisomers/anomers was **2α**:**2β** = 58:42 and **3α**:**3β** = 23:77.

Pyridine mediated peracetylation of xylose **(Table 4, entry 9)**. α-D-xylose (**1**) (2.00 g, 13.32 mmol) was added to a 100 mL round bottom flask under N_2. CH_2Cl_2 (10 mL), pyridine (9 mL, 106.56 mmol) and Ac_2O (9 mL, 93.25 mmol) were added to the flask and the white suspension was stirred at 25 ˚C for 2 hours. After 2 hours, the clear yellow solution was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes. The solution was transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a colorless, clear oil (3.55 g, 84%). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained both **2α/β** and **3α/β** in a ratio of 95:5 while the ratio of **2β** to **2α/3α/3β** was 31:69. The ratio of stereoisomers/anomers was **2α**:**2β** = 68:32 and **3α**:**3β** = 57:43. ^{1}H NMR ($CDCl_3$): key resonances of four products δ: 6.42 (d, *J* = 4.4, H-1of 3α), 6.25 (d, *J* = 4.0, H-1of 2α), 6.10 (s, H-1 of 3β), 5.70 (d, *J* = 6.8, H-1 of 2β), 5.45 (t, *J* = 10.0, H-3 of 2α), 5.19 (t, *J* = 8.0, H-3 of 2β), 5.02 (m, H-2 of 2α/2β and H-4 of 2α/2β), 3.92 (dd, *J* = 10.8, 6.0, H-5 of 2α), 3.70 (t, *J* = 10.8, H-5'of 2α).

NEt_3 mediated peracetylation of arabinose **(Table 5, entry 1)**. α-L-arabinose (**4**) (2.00 g, 13.32 mmol) was added to a 100 mL round bottom flask under N_2. CH_2Cl_2 (10 mL) and NEt_3 (15 mL, 106.56 mmol) were added to the flask and the white suspension was stirred at 25 ˚C. The flask was cooled to 0 ˚C and stirred for 10 minutes. Ac_2O (9 mL, 93.25 mmol) was added dropwise to the flask. The white suspension was stirred at 0 ˚C for 4 hours. After 4 hours, the solution was still a white suspension and the

flask was removed from the ice bath and warmed to 25 ˚C. The reaction mixture was stirred at 25 ˚C for 2 hours. After 2 hours, the clear yellow solution was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes and the bi-phasic, yellow suspension was stirred for 12 hours. The solution was transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a yellow glass (3.30 g, 78%). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained both **5α/β** and **6α/β** in a ratio of 67:33. The ratio of stereoisomers/anomers was **5α**:**5β** = 9:91 and **6α**:**6β** = 44:56. No attempt was made to isolate pure β

NEt_3 mediated peracetylation of arabinose **(Table 5, entry 3)**. α-L-arabinose (**4**) (2.00 g, 13.32 mmol) was added to a 100 mL round bottom flask under N_2. CH_2Cl_2 (10 mL), NEt_3 (15 mL, 106.56 mmol) and Ac_2O (9 mL, 93.25 mmol) were added to the flask, where the white suspension warmed to the touch. The white suspension was stirred at 25 ˚C for 4 hours. After 4 hours, the clear yellow solution was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes. The solution was transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a yellow glass (3.47 g, 88%). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained both **5α/β** and **6α/β** in a ratio of 70:30. The ratio of stereoisomers/anomers was **5α**:**5β** = 7:93 and **6α**:**6β** = 43:57. No attempt was made to isolate pure β arabinopyranose due to a higher ratio of arabinofuranose in the reaction mixture.

NEt_3 mediated peracetylation of 5:1 pentose mixture **(Table 6, entry 1)**. A 5:1 (m/m) mixture of commercially obtained **1** and **4** (2.00 g, 13.32 mmol) was added to a 100 mL round bottom flask under N_2. CH_2Cl_2 (10 mL), NEt_3 (15 mL, 106.56 mmol) and Ac_2O (9 mL, 93.25 mmol) were added to the flask, where the white suspension warmed to the touch. The white suspension was stirred at 25 ˚C for 1.5 hours where the solids reached dissolution. After 2 hours, the clear yellow solution was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes. The solution was transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a white crystalline solid (3.2 g). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained peracetylated D-xylose and L-arabinose in a ratio of 81:19 (4.3:1), xyloses **2α/β** and **3α/β** in a ratio of 93:7 and arabinoses **5α/β** and **6α/β** in a ratio of 72:28. The ratio of **2β** to **2α/3/5/6** was 66:34. Absolute EtOH (50 mL) was added to the crystals. The crystals dissolved in EtOH when the solution was heated. The solution volume was reduced to 30 mL with heating. The flask was then removed from heat and allowed to cool to 25 ˚C. The solution was chilled in an ice bath which yielded white crystals. The crystals were collected by filtration and dried to afford a white, crystalline solid (1.58g, 45%), mp 120-122 ˚C (lit.[29] 125-128 ˚C). The solid was characterized by ^{1}H NMR ($CDCl_3$) and identified as **2β**. ^{1}H NMR characterization of the crystallization filtrate in $CDCl_3$ showed the ratio of **2β** to **2α/3/5/6** had changed to 18:82.

NEt_3 mediated peracetylation of 5:1 pentose mixture **(Table 6, entry 2)**. A 5:1 (m/m) mixture of extracted **1** and **4** (2.00 g, 13.32 mmol) was added to a 100 mL round bottom flask under N_2. CH_2Cl_2 (10 mL), NEt_3 (15 mL, 106.56 mmol) and Ac_2O (9 mL, 93.25 mmol) were added to the flask. The white suspension was stirred at 25 ˚C for 30 minutes where the solids reached dissolution. After 4 hours, the clear yellow solution was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath

was removed after 20 minutes. The solution was transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a white crystalline solid mixed with yellow oil (4.11 g). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained peracetylated D-xylose and L-arabinose in a ratio of 81:19 (4.3:1), xyloses **2α/β** and **3α/β** in a ratio of 94:6 and arabinoses **5α/β** and **6α/β** in a ratio of 75:25. The ratio of **2β** to **2α/3/5/6** was 68:32. Absolute EtOH (60 mL) was added to the crystals. The mixture was stirred and heated to dissolve all solids. The solution volume was then reduced to 30 mL with heating. The flask was removed from heat and allowed to cool to 25 ˚C. The solution was chilled in an ice bath and agitated which yielded white crystals. The crystals were collected by filtration and dried to afford a white, crystalline solid (2.01 g, 47%), mp 121-122 ˚C (lit.[29] 125-128 ˚C). The solid was characterized by ^{1}H NMR ($CDCl_3$) and identified as **2β**. ^{1}H NMR characterization of the crystallization filtrate in $CDCl_3$ showed the ratio of **2β** to **2α/3/5/6** had changed to 24:76.

NEt_3 mediated peracetylation of 5:1 pentose mixture **(Table 6, entry 3)**. A 5:1 mass (m/m) mixture of extracted **1** and **4** (2.00 g, 13.32 mmol) was added to a 100 mL round bottom flask under N_2. CH_2Cl_2 (10 mL), NEt_3 (15 mL, 106.56 mmol) and Ac_2O (9 mL, 93.25 mmol) were added to the flask. The white suspension was stirred at 25 ˚C for 1 hour where the solids reached dissolution. After 2 hours, the clear yellow solution was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes. The solution was transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield a yellow oil (3.69 g). Crystals then grew from

the isolated oil after drying under dynamic N_2 and agitation. ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained peracetylated D-xylose and L-arabinose in a ratio of 78:22 (3.6:1), xyloses **2α/β** and **3α/β** in a ratio of 93:7 and arabinoses **5α/β** and **6α/β** in a ratio of 71:29. The ratio of **2β** to **2α/3/5/6** was 63:37. Absolute EtOH (60 mL) was added to the crystals. The mixture was stirred and heated to dissolve all solids. The solution volume was then reduced to 30 mL with heating. The flask was removed from heat and allowed to cool to 25 ˚C. The solution was chilled in an ice bath and agitated which yielded white crystals. The crystals were collected by filtration and dried to afford a white, crystalline solid (1.71 g, 40 %), mp 121-123 ˚C (lit.[29] 125-128 ˚C). The solid was characterized by ^{1}H NMR ($CDCl_3$) and identified as **2β**. ^{1}H NMR characterization of the crystallization filtrate in $CDCl_3$ showed the ratio of **2β** to **2α/3/5/6** had changed to 20:80.

DMAP/NEt_3 mediated peracetylation of 4.4:1 pentose mixture **(Table 7, entry 1)**. A 4.4:1 (m/m) mixture of commercially obtained **4** and **1** (2.00 g, 13.32 mmol) and DMAP (0.17 g, 1.33 mmol) were added to a 100 mL round bottom flask under N_2. CH_2Cl_2 (10 mL) and NEt_3 (15 mL, 106.56 mmol) were added to the flask and the white suspension was stirred at 25 ˚C. The flask was cooled to 0 ˚C and stirred for 10 minutes. Acetic anhydride (9 mL, 93.25 mmol) was added dropwise to the flask. The white suspension was stirred at 0 ˚C for 2 hours. After 2 hours, the clear, yellow solution was removed from the ice bath and warmed to 25 ˚C. The solution was stirred at 25 ˚C for 2 hours. After 2 hours, the solution flask was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes and the bi-phasic, yellow solution was stirred overnight. The solution was transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield of a yellow crystalline solid (4.15 g). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained peracetylated L-arabinose and D-xylose in a ratio of 81:19 (4.3:1). The reaction

mixture contained arabinoses **5** and **6** in a ratio of 94:6 and only contained xylopyranoses **2**. The ratio of **5α** to **5β/2/6** was 74:26. The ratio of arabinose stereoisomers/anomers was **5α**:**5β** = 98:2 and **6α**:**6β** = 71:29 and the ratio of xylopyranoses was **2α/β** = 92:8. The yellow solid was broken up with a spatula and 0 ˚C 1-propanol (5 mL) was added. The slush was kept in an ice bath for 20 minutes and white solid collected by filtration, washed with 10 mL of 0 ˚C 1-propanol and dried to afford a white solid (1.79 g, 42 %), mp 95.5-97 ˚C. The solid was characterized by ^{1}H NMR ($CDCl_3$) and identified as **5α**. ^{1}H NMR characterization of the crystallization filtrate in $CDCl_3$ showed the ratio of **5α** to **5β/2/6** had changed to 53:47.

DMAP/NEt$_3$ mediated peracetylation of 4.4:1 pentose mixture **(Table 7, entry 2)**. A 4.4:1 (m/m) mixture of commercially obtained **4** and **1** (2.00 g, 13.32 mmol) and DMAP (0.17 g, 1.33 mmol) were added to a 100 mL round bottom flask under N_2. CH_2Cl_2 (10 mL) and NEt_3 (15 mL, 106.56 mmol) were added to the flask and the white suspension was stirred at 25 ˚C. The flask was cooled to 0 ˚C and stirred for 10 minutes. Acetic anhydride (9 mL, 93.25 mmol) was added dropwise to the flask. The white suspension was stirred at 0 ˚C for 2 hours. After 2 hours, the clear, yellow solution was removed from the ice bath and warmed to 25 ˚C. The solution was stirred at 25 ˚C for 2 hours. After 2 hours, the solution flask was placed in an ice bath and quenched with chilled DI water (20 mL). The ice bath was removed after 20 minutes and the bi-phasic, yellow solution was stirred overnight. The solution was transferred to a 250 mL separatory funnel, washed with CH_2Cl_2 (3 x 20 mL) and the organic layer from each wash was collected. The combined organic layer (CH_2Cl_2) was then washed with 1M HCl (4 x 20 mL), chilled DI water (3 x 20 mL), saturated $NaHCO_3$ (3 x 20 mL), and chilled DI water (2 x 20 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, filtered through celite, and the solvent was removed under vacuum to yield of a yellow crystalline solid (4.2 g). ^{1}H NMR characterization of the isolated reaction mixture in $CDCl_3$ showed it contained peracetylated L-arabinose and D-xylose in a ratio of 81:19 (4.3:1). The reaction mixture contained arabinoses **5** and **6** in a ratio of 94:6 and only contained xylopyranoses **2**. The ratio of **5α** to **5β/2/6** was 75:25. The ratio of arabinose stereoisomers/anomers was **5α**:**5β** = 98:2 and **6α**:**6β** =

71:29 and the ratio of xylopyranoses was **2α/β** = 92:8. The yellow solid was broken up with a spatula and 0 ˚C 1-propanol (9 mL) was added. The slush was kept in an ice bath for 30 minutes and white solid collected by filtration, washed with 10 mL of 0 ˚C 1-propanol and dried to afford a white solid (1.69 g, 40 %), mp 96-97 °C. The solid was characterized by ^{1}H NMR ($CDCl_3$) and identified as **5α**. ^{1}H NMR characterization of the crystallization filtrate in $CDCl_3$ showed the ratio of **5α** to **5β**/**2**/**6** had changed to 55:45.

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Supplementary Material

Supplementary data associated with this article can be found in the online version at #####. This includes NMR data for compounds presented in this paper.

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- Stereoselective peracetylation of α-D-xylopyranose and α-L-arabinose is described.
- ^{1}H NMR characterization of α-D-xylopyranose and α-L-arabinose was obtained.
- ^{1}H NMR characterization of all peracetylated products was obtained.
- Peracetylation was used to separate mixtures of D-xylose and L-arabinose.