Conversion of Pyranose Glycals to Furanose Derivatives: A New Route to Oligofuranosides

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Received July 31, 1998

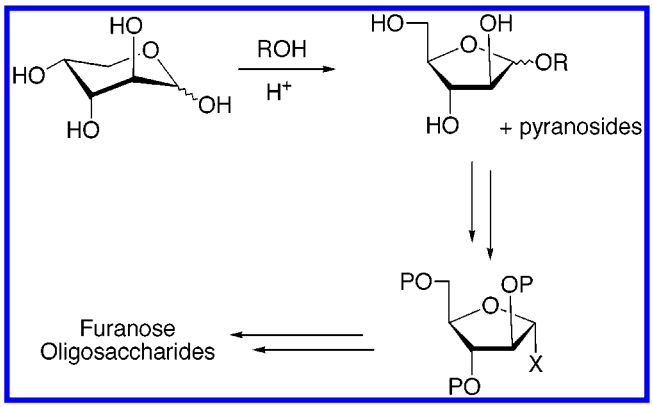
Acetylated pyranose glycals have been converted through a convenient three-step process into protected furanose reducing sugars. Ozonolysis of 2,3,5-tri-*O*-acetyl-glucal or 2,3,5-tri-*O*-acetyl-galactal, followed by treatment with dimethyl sulfide and then hydrolysis gave respectively protected arabinofuranose (**6**) and lyxofuranose (**7**) derivatives. Conversion of these hemiacetals to oligosaccharides was explored using a number of methods. Activation of **6** or **7** in situ afforded glycosides in modest yield and stereoselectivity. Glycosylation of tetraacetates **16** and **18**, obtained from **6** and **7**, gave similar results. However, thioglycosides **17** and **19**, also derived from **6** and **7**, were found to be effective glycosyl donors, producing products in good to excellent yields and with high stereoselectivities. The method was also used to synthesize a disaccharide in which one residue contained uniform ^{13}C enrichment.

Introduction

Oligosaccharides containing furanose moieties are important constituents of a number of lower organisms including bacteria,[1] parasites,[2] fungi,[3] and plants.[4] The most spectacular examples of these glycans are found in mycobacteria, including *Mycobacterium tuberculosis*. An integral constituent of the protective cell wall of this organism is an arabinogalactan in which all of the arabinose and galactose residues exist in the furanose form.[1] Because furanose oligosaccharides are unknown in humans and, at the same time, are critical for the survival of mycobacteria and other pathogenic organisms, the enzymes that assemble them are ideal targets for drug action. Consequently, there has been increasing interest in the synthesis of furanose oligosaccharides and related analogues that could act as either glycosyltransferase substrates[5] or inhibitors.[6] However, in comparison with their pyranosidic counterparts, there has been relatively little work directed toward synthesizing oligofuranosides.

The majority of free hexoses and pentoses exist predominately in the pyranose form, and the preparation of furanosides is most often achieved by subjecting an unprotected reducing sugar to a controlled Fisher glycosylation reaction (Scheme 1).[7] The furanosides are the kinetic products, and at short reaction times modest to good yields of these isomers are obtained. Methyl glycosides are typically synthesized by this approach, and conversion to a derivative (e.g., glycosyl halide, thioglycoside) suitable for oligosaccharide synthesis requires further manipulation. Recently, both Fraser-Reid[8] and Plusquellec[9] have reported that Fisher glycosylation of hexoses with 4-penten-1-ol yields glycosides that can, after protection of the hydroxyl groups, be used directly in glycosylation reactions. A related approach is the high-temperature acylation of unprotected sugars to generate a fully acylated furanose that can be used as a glycosyl donor upon activation with a Lewis acid.[10] A disadvantage of these approaches is that yields are variable from sugar to sugar, and the reaction mixtures are sometimes contaminated with pyranose isomers which complicate purification. An alternative method

Scheme 1[a]



[a] P = protecting group; X = activatable group.

(1) Brennan, P. J.; Nikaido, H. *Annu. Rev. Biochem.* **1995**, *64*, 29.
(2) (a) Gerold, P.; Eckert, V.; Schwarz, R. T. *Trends Glycosci. Glycotechnol.* **1996**, *8*, 265. (b) de Lederkremer, R. M.; Colli, W. *Glycobiology* **1995**, *5*, 547.
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(6) (a) Bouix, C. B.; Bisseret, P.; Eustache, J. *Tetrahedron Lett.* **1998**, *39*, 825. (b) Maddry, J. A.; Bansal, N.; Bermudez, L. E.; Comber, R. N.; Orme, I. M.; Suling, W. J.; Wilson, L. N.; Reynolds, R. C. *Tetrahedron Lett.* **1998**, *39*, 237. (c) Lee, R. E.; Smith, M. D.; Nash, R. J.; Griffiths, R. C.; McNeil, M.; Grewal, R. K.; Yan, W.; Besra, G. S.; Brennan, P. J.; Fleet, G. W. J. *Tetrahedron Lett.* **1997**, *38*, 6733.
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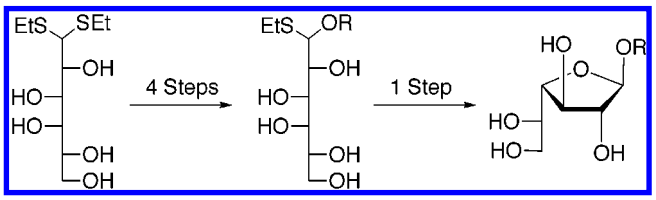
10.1021/jo9815406 CCC: $15.00
Published on Web 11/06/1998

Scheme 2



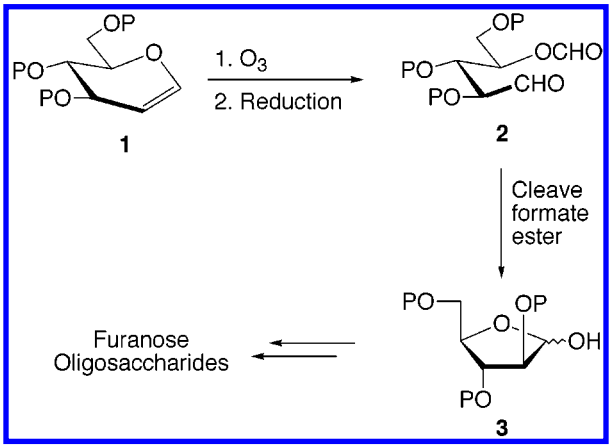
(Scheme 2) involves the conversion of sugar dithioacetals to mixed S,O acetals and then cyclization to furanosidic glycosides. This method was developed over 50 years ago by Wolfrom for the synthesis of furanosides of simple alcohols;[7,11] more recently it has been applied to the preparation of oligosaccharides.[12] This route provides furanosides in the absence of pyranosides; however, a number of steps are required to carry out this transformation.

As part of a program directed at the synthesis of furanose oligosaccharides, we were interested in developing alternate routes to furanose monosaccharides that could be converted to suitable glycosylating agents. We demonstrate here that acetylated pyranose glycals can be converted efficiently to furanose glycosyl donors and, in turn, oligosaccharides.

Results and Discussion

Pyranose glycals are readily accessible synthetic intermediates, and many are commercially available. These versatile compounds have been used widely in organic synthesis for the preparation of oligosaccharides,[13] C-glycosides,[14] and other natural products.[15] It occurred to us (Scheme 3) that ozonolysis of a protected pyranose

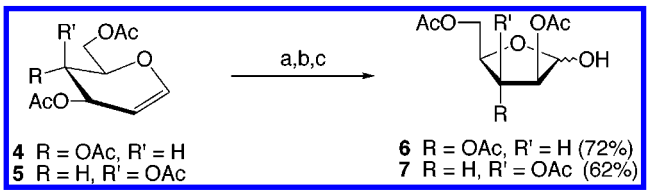
Scheme 3[a]



[a] P = protecting group.

glycal (**1**) followed by a reductive workup and selective cleavage of the resulting formate ester (**2**) would produce a hydroxy−aldehyde that would spontaneously cyclize to give a protected furanose derivative (**3**). This route offers advantages over the Fisher glycosylation process in that (1) pyranoside formation is not a possible side reaction and (2) the product formed is already protected and can be activated either directly or indirectly and used as a glycosyl donor. Furthermore, in contrast to the dithioacetal cyclization route to furanosides, we envisioned that it would be possible to carry out the conversion of **1** into **3** without purification of the intermediate, hence adding to the overall efficiency of the process.

Scheme 4[a]



[a] (a) O_3, $NaHCO_3$, CH_2Cl_2, CH_3OH, −78 °C. (b) $(CH_3)_2S$, −78 °C → rt. (c) HOAc, CH_3OH (3:2), 70 °C.

Synthesis of Protected Furanose Reducing Sugars. Relatively few reports describe the ozonolysis of glycals. Reiser and co-workers[16] have reported that ozonolysis of tri-*O*-acetyl-D-glucal (**4**) followed by treatment with acetic anhydride and triethylamine affords a 4-formyloxy-D-arabinonic acid methyl ester derivative. Similarly, tri-*O*-benzyl-D-glucal has been converted to 2,3,5-tri-*O*-benzyl-4-formyloxy-D-arabinose (**2**, P = Bn) upon treatment with ozone followed by dimethyl sulfide.[17]

As illustrated in Scheme 4, ozonolysis of **4** in a mixture of methanol and dichloromethane in the presence of sodium bicarbonate[16] was followed by treatment with dimethyl sulfide to give a formyl aldehyde (Scheme 3, **2**, P = Ac). This product was not purified but rather the reaction mixture was evaporated, dissolved in methanol, filtered, and re-evaporated to give a residue that was heated overnight in acetic acid/methanol (3:2) at 70 °C. Under these conditions, the formate ester was selectively cleaved, thus producing 2,3,5-tri-*O*-acetyl-D-arabinofuranose (**6**) in 72% yield from **4** after chromatography. A similar sequence of reactions was carried out on tri-*O*-acetyl-D-galactal (**5**) to give the D-lyxofuranose analogue **7** in 62% overall yield.

The conversion of **4** into **6** through the use of an in situ dihydroxylation/oxidative cleavage protocol was also investigated. However, treatment of **4** with osmium tetroxide and sodium periodate, as reported for 3,4-di-*O*-acetyl-D-xylal,[18] gave low product yields and significant amounts of unreacted starting material. A number of reaction conditions were also explored for the cleavage of the formate ester including silica gel in methanol,[19] refluxing methanol,[20] and morpholine,[16] but all gave results inferior to the described mixture of acetic acid and methanol.

Glycosylation Reactions. We had hoped that in situ activation of the hydroxyl group would enable us to construct glycosides directly from hemiacetals **6** and **7** (Scheme 5). While such methods are available,[21] most involve donors containing alkyl protecting groups and thus are activated relative to **6** and **7**. Nevertheless, we

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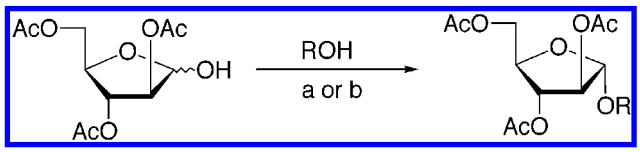
Scheme 5[a]



[a] (a) $Yb(OTf)_3$, $CH_3OCH_2CO_2H$. (b) Tf_2O, Ph_2SO, 2-chloropyridine.

Table 1. Glycosylation of 6, 7, and 16−19

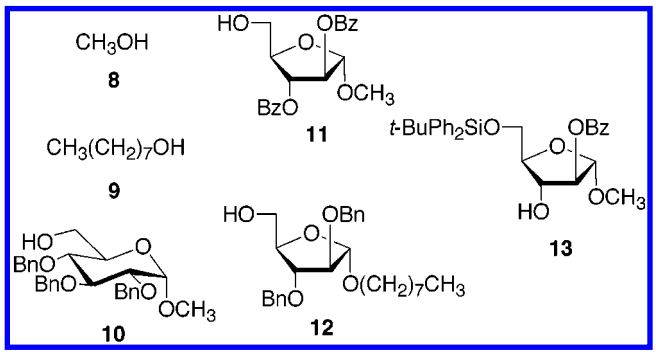
entry	donor	ROH[a]	conditns[b]	yield (%)[c]	α:β ratio[d]	product
1	**6**	**8**	A[e]	49	10:1	**20**
2	**6**	**9**	A	37	10:3	**22**
3	**6**	**10**	A	21	2:1	**23**
4	**6**	**8**	B	45	α	**20**
5	**6**	**9**	B	50	20:3	**22**
6	**6**	**10**	B	19	4:1	**23**
7	**7**	**10**	A	NR[g]		**24**
8	**7**	**10**	B	10	α	**24**
9	**16**	**10**	C	21	2:1	**23**
10	**18**	**10**	C	62	3:1	**24**
11	**17**	**8**	D[f]	65	α	**20**
12	**17**	**9**	D	54	α	**22**
13	**17**	**10**	D	82	α	**23**
14	**17**	**11**	D	86	α	**25**
15	**17**	**13**	D	79	α	**28**
16	**19**	**8**	D[f]	71	α	**21**
17	**19**	**10**	D	85	α	**24**
18	**19**	**11**	D	69	α	**26**
19	**19**	**12**	D	76	α	**27**
20	**19**	**13**	D	65	α	**29**

[a] For **8** and **9**, 3−5 equiv of alcohol was added relative to donor; for **10**−**13**, 1.0−1.2 equiv. [b] A. donor (1.0 equiv), ROH, $CH_3OCH_2CO_2H$ (1.0 equiv), $Yb(OTf)_3$ (0.2 equiv), CH_2Cl_2, reflux. B. donor (1.0 equiv), ROH, Ph_2SO (2.8 equiv), Tf_2O (1.4 equiv), 2-chloropyridine (5.0 equiv), −40 °C → rt. C. donor (1.0 equiv), ROH, $SnCl_4$ (1.0 equiv), rt. D. donor (1.0 equiv), ROH, NIS (1.3 equiv), AgOTf (0.3 equiv), 0 °C. [c] Isolated yield after chromatography. [d] Ratio determined by ^1H NMR of chromatographed product. [e] Reaction carried out at rt. [f] Reaction done in CH_3CN. [g] No reaction observed; see text.

explored this possibility by first attempting the glycosylation of **6** with alcohols **8**−**10** using a method reported by Inanga and co-workers.[21a] Upon treatment of **6** with these alcohols under the described conditions (methoxy acetic acid in a refluxing solution of dichloromethane containing catalytic ytterbium triflate), only modest yields of the glycosides were obtained (Table 1, entries 1−3). Furthermore, significant quantities of the 1,2-*cis*-glycosides were produced. Separation of these products proved impossible because of their identical chromatographic properties.

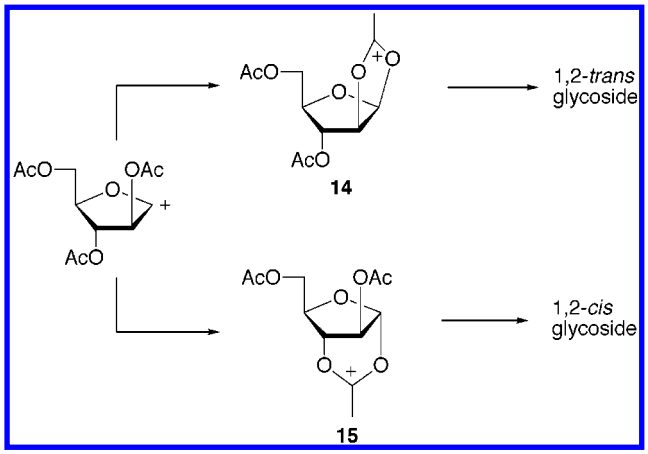
We next investigated a recently reported method involving direct activation of the anomeric center by diphenyl sulfoxide and triflic anhydride in the presence of 2-chloropyridine[22] (Scheme 5). This method has been shown to give excellent yields for both alkylated and acylated pyranose reducing sugars; when O-2 is acylated, the 1,2-*trans*-glycosides are formed exclusively. However, again, glycosylation of alcohols **8**−**10** with **6** gave modest product yields. Although the stereoselectivities were better with some alcohols, with others, inseparable mixtures were still produced (Table 1, entries 4−6).

Scheme 6



Given that **6** contains an acetyl protecting group on O-2, it was expected that only the 1,2-*trans*-glycosides would be formed through intermediate **14** because of neighboring group participation (Scheme 7). We were therefore initially surprised when significant amounts of the 1,2-*cis*-glycosides were formed. However, the formation of β-glycosides as byproducts in the glycosylation of acylated arabinofuranose derivatives has been previously described.[23] For example, Lewis acid promoted glycosylation of a number of alcohols by tetraacetate **16** has been reported to give almost equal amounts of both glycoside anomers in low yields.[23b] A plausible explanation (Scheme 7) for the erosion of stereocontrol is that there is participation underneath the ring by the acyl group on O-3 giving intermediate **15**, which in turn would lead to the β-arabinofuranoside. Such participation has previously been invoked and used to advantage in the synthesis of 2-deoxy β-D-nucleosides and C-glycosides.[24]

Scheme 7



To investigate this possibility, we then examined the glycosylation of the lyxofuranose derivative **7**. If participation of the protecting group on O-3 is a major factor in determining the stereochemical outcome of glycosylations with **6**, then **7** should give higher stereoselectivities. Unfortunately, reaction of **7** with **10** failed to give any product in the case of one activating system and gave only very low yields of product in the other (Table 1, entries 7 and 8). In both cases, even at long reaction times and with the addition of more promoter, significant

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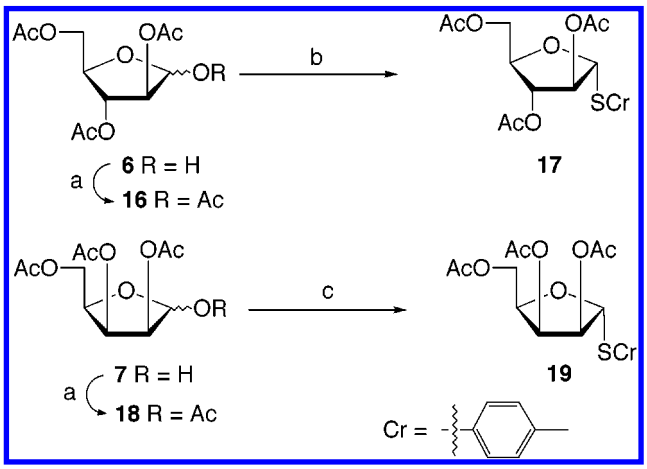
Scheme 8[a]



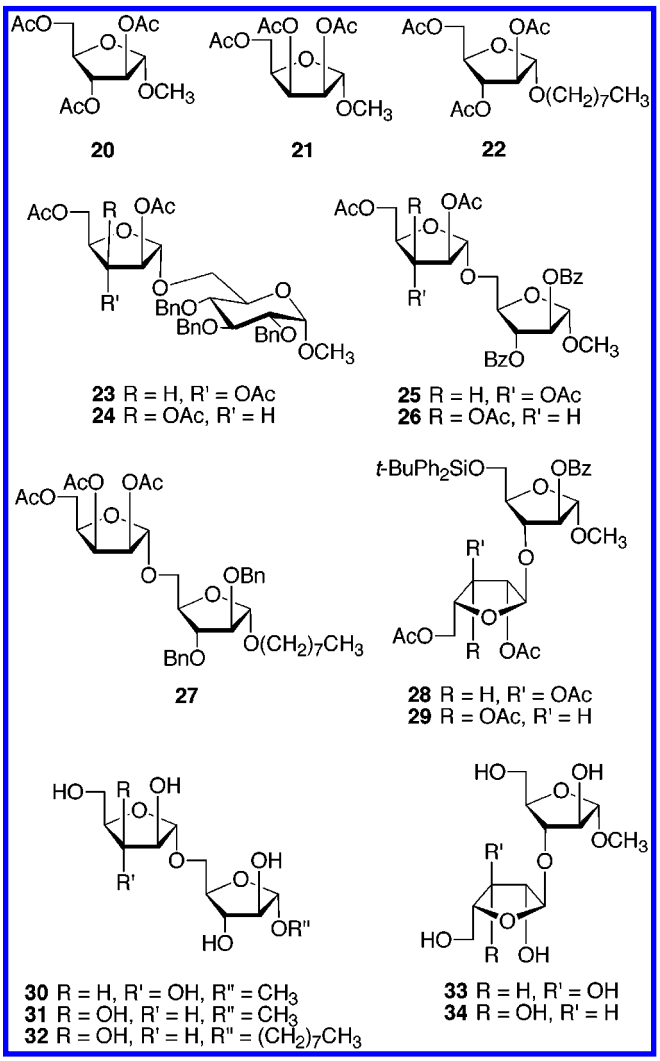
[a] (a) Ac_2O, H_2SO_4, 0 °C, 99%. (b) CrSH, BF_3OEt_2, 0 °C, 85%. (c) CrSH, BF_3OEt_2, 0 °C, 80%.

amounts of unreacted starting materials were recovered. Although the use of the diphenyl sulfoxide/triflic anhydride promoter system gave the product with excellent stereocontrol, the low yields prompted us to explore other glycosyl donors. We then synthesized tetraacetates **16** and **18** from **6** and **7**, respectively (Scheme 8). Reaction of both donors with alcohol **10** in the presence of tin(IV) chloride gave mixtures of glycosides (Table 1, entries 9 and 10). In the case of the lyxo analogue **18**, the selectivity for the α product was slightly greater than that in the arabino analogue **16**. However, the formation of substantial amounts of the *β*-glycoside from **18** suggests that while participation under the ring by a protecting group on O-3 may contribute to poor glycosylation stereocontrol with some arabinose donors (e.g., **6** and **16**), it is not the only factor.

We then turned our attention to activation of these sugars indirectly by way of thioglycosides **17** and **19**. The former has previously been shown to efficiently glycosylate both primary and secondary carbohydrate alcohols.[5a] The required thiocresyl donors were synthesized from **16** and **18** without incident in 80−85% yield (Scheme 8). Glycosylation of alcohols **8**−**13** with either **17** or **19** gave the desired products in good to excellent yields with high stereoselectivities; none of the 1,2-*cis*-glycoside was detected (Table 1, entries 11−20). The lowest yield obtained, 54%, was in the glycosylation of octanol (entry 12), which could possibly be due to the formation of the 1,2-*cis*-glycoside. However, as both anomers of this octyl glycoside have identical chromatographic mobilities, the formation of the undesired *β*-glycoside would have been readily apparent in the NMR spectrum of the isolated product; none was detected. The protected disaccharides **25**−**29** (Scheme 9) were then deprotected using standard methods to afford oligosaccharides **30**−**34**. Compounds **30** and **33** have been shown to be substrates for mycobacterial arabinosyltransferases,[5a] while **31**, **32**, and **34** are potential substrates for the same enzymes.

Synthesis of ^{13}C-Labeled Arabinofuranosides. Isotopically enriched carbohydrates are of increasing importance in oligosaccharide conformational studies,[25] and the method reported here will be especially useful in preparing glycans containing labeled arabinofuranosyl residues. We have used this method for the synthesis of a disaccharide in which one residue is ^{13}C-enriched

Scheme 9



(Scheme 10). D-Glucose, uniformly ^{13}C-enriched at levels of 99% (**35**), was converted to the known[26] glucal **36** in 85% yield using a convenient one-pot procedure.[27] Ozonolysis of the glycal and hydrolysis gave **37** which was converted to thioglycoside **38** as outlined in Schemes 4 and 8 for the unlabeled parent. Glycosylation of alcohol **11** with **38** provided the disaccharide **39**, which was deacylated to give **40**, a labeled analogue of **30**.

This approach to **40** is more efficient than the traditional route which would involve Fisher glycosylation of 99% uniformly enriched D-arabinose and subsequent conversion to the disaccharide. In addition to being faster, 99% uniformly labeled D-arabinose is considerably more expensive than similarly enriched D-glucose. In addition to its utility in oligosaccharide synthesis, **38** should also be a valuable intermediate in the synthesis of ^{13}C-labeled arabinonucleosides. An intermediate suitable for the preparation of uniformly ^{13}C-enriched ribonucleosides has been recently reported, also starting from labeled D-glucose.[28]

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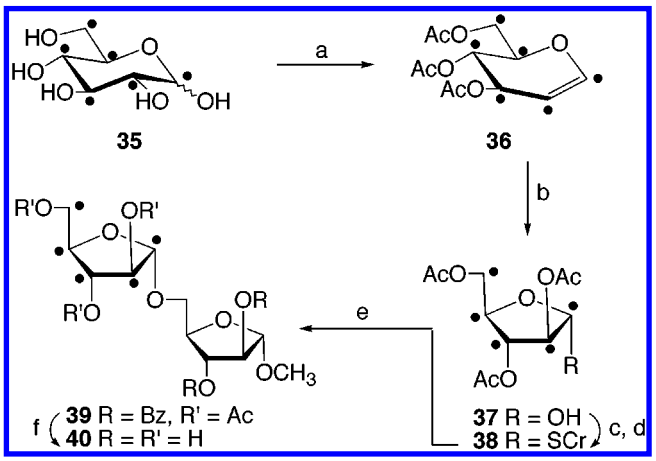
Scheme 10[a]



[a] (a) Reference 27. (b) Scheme 4. (c) Ac_2O, H_2SO_4, 0 °C. (d) CrSH, BF_3OEt_2, 0 °C. (e) **11**, NIS, AgOTf, CH_2Cl_2, 0 °C. (f) $NaOCH_3$, CH_3OH.

In conclusion, we have developed a new synthetic route to protected furanose sugars that can be activated and converted to oligosaccharides. The formation of pyranoses is not a possible side reaction, and therefore this route has advantages over the usual methods for furanoside synthesis. We have demonstrated the utility of this approach by the preparation of two of the four possible 2,3,5-tri-*O*-acetyl-pentofuranoses. The method should be readily applied to the other isomers by starting with the appropriate protected glycal. The possibility of using this route to synthesize a variety of isotopically enriched arabinofuranosides from glucose is especially appealing as labeled glucose derivatives are straightforwardly obtained.[29] For example, in addition to uniformly ^{13}C-enriched D-glucose, all of the singly ^{13}C-labeled derivatives are commercially available, as are a host of deuterated analogues.[30] Arabinofuranose residues are among the most common of all pentofuranoses present in naturally occurring oligosaccharides, and this methodology will allow rapid access to these derivatives in both their labeled and unlabeled forms.

Finally, the poor stereocontrol observed with donors **6**, **7**, **16**, and **18** is worthy of mention and further study. In pyranose systems, a variety of 2-*O*-acylated glycosyl donors reliably provide 1,2-*trans*-glycosides.[31] However, it appears that at least with some furanoses product ratios in glycosylation reactions are much more sensitive to the choice of donor and activation method. We are currently further investigating the use of these and other glycosylating agents for the synthesis of oligofuranosides.

Experimental Section

General Methods. Solvents were distilled from the appropriate drying agents before use. Unless stated otherwise, all reactions were carried out at room temperature under a positive pressure of argon and were monitored by TLC on silica gel 60 F_{254} (0.25 mm, E. Merck). Spots were detected under UV light or by charring with 10% H_2SO_4 in EtOH. Solvents were evaporated under reduced pressure and below 40 °C (bath). Solutions of crude products were dried over anhydrous Na_2SO_4. Column chromatography was performed on silica gel 60 (40−60 μM). The ratio between silica gel and crude product ranged from 100:1 to 50:1 (w/w). Optical rotations were measured at 22 ± 2 °C. ^1H NMR spectra were recorded at 300 or 600 MHz, and chemical shifts are referenced to either TMS (0.0, $CDCl_3$) or HOD (4.78, D_2O). ^{13}C NMR spectra were recorded at 75.5 or 125 MHz, and ^{13}C chemical shifts are referenced to internal $CDCl_3$ (77.00, $CDCl_3$) or external dioxane (67.40, D_2O). Yields for the glycosylation reactions are given in Table 1. The assignment of resonances of deprotected compounds **30**−**34** was made by two-dimensional homonuclear and heteronuclear shift correlation experiments. Assignments of R and S to the protons attached to C5 were made by comparison of $^3J_{H4,H5}$ values with those previously reported.[32] The ^1H NMR spectra of the ^{13}C-labeled compounds (**38**−**40**) were complicated by $^{13}C/^1H$ couplings. However, the proton-decoupled ^{13}C NMR spectra of these compounds were readily interpreted by comparison with the spectra of the unlabeled parents (**17**, **25**, and **30**); signal multiplicities due to $^{13}C/^{13}C$ coupling were as expected. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. Fast atom bombardment mass spectra were recorded on samples suspended in Cleland's matrix using a cesium gun.

Representative Procedure for Ytterbium Triflate/Methoxy Acetic Acid Promoted Glycosylations. To a solution of **6** (84 mg, 0.30 mmol) in dry CH_2Cl_2 (10 mL) were added successively 1-octanol (144 μL, 0.91 mmol), methoxy acetic acid (23 μL, 0.30 mmol), and $Yb(OTf)_3$ (38 mg, 0.06 mmol). The mixture was refluxed for 2.5 h under argon through a column of activated 4 Å molecular sieves. The mixture was cooled to room temperature, diluted with CH_2Cl_2, and then washed with a saturated solution of $NaHCO_3$. The solution was then dried and chromatographed (hexane/EtOAc, 1:1) to give the product **22** (44 mg, 37%) as a syrup.

Representative Procedure for Triflic Anhydride/Diphenyl Sulfoxide Promoted Glycosylations. To a stirred mixture of compound **6** (56 mg, 0.2 mmol) and diphenyl sulfoxide (115 mg, 0.57 mmol) in a mixture of toluene and CH_2Cl_2 (3:1, 8 mL) at −78 °C was added dropwise triflic anhydride (48 μL, 0.28 mmol). The reaction mixture was stirred at this temperature for 20 min and then at −40 °C for 1 h. 2-Chloropyridine (96 μL, 1.01 mmol) and **10** (113 mg, 0.24 mmol) were added at −40 °C. The solution was stirred at this temperature for 1 h, then at 0 °C for 20 min, and finally at room temperature for 12 h before the addition of excess Et_3N (0.22 mL, 1.58 mmol). The mixture was diluted with CH_2Cl_2 and washed with saturated solutions of $NaHCO_3$ and NaCl. The organic phase was dried, filtered, concentrated, and purified by chromatography (hexane/EtOAc, 1:1) to give **23** (28 mg, 19%) as a syrup.

Representative Procedure for Thioglycoside Glycosylations. A mixture of **19** (73 mg, 0.19 mmol), alcohol **12** (77 mg, 0.17 mmol), powdered molecular sieves (4 Å, 0.5 g), and dry CH_2Cl_2 (10 mL) was stirred at 0 °C for 20 min. To the mixture were added *N*-iodosuccinimide (56 mg, 0.25 mmol) and silver triflate (15 mg, 0.06 mmol). After being stirred for 2 h, the reaction was quenched with Et_3N, and the reaction mixture was diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed successively with a saturated solution of $Na_2S_2O_3$, water, and a saturated NaCl solution. After the filtrate was dried, the solvent was evaporated, and the residue was chromatographed (hexanes/EtOAc, 1:1) to yield the disaccharide **27** (93 mg, 76%) as a colorless syrup.

Representative Procedure for Peracetate Glycosylations. To a stirred solution of **18** (52 mg, 0.16 mmol) in dry CH_3CN (5 mL) was added $SnCl_4$ (19 μL, 0.16 mmol) dropwise at room temperature. After 20 min, a solution of **10** (55 mg, 0.12 mmol) in CH_3CN (3 mL) was added dropwise. After 1 h of stirring, the mixture was cooled to 0 °C, and a saturated

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$NaHCO_3$ solution (2 mL) was added to precipitate tin salts. The reaction mixture was diluted with CH_2Cl_2 and filtered through Celite, and the filtrate was washed with water and a saturated NaCl solution. After the filtrate was dried and concentrated, the crude product was purified by chromatography (hexane/EtOAc, 3:1) to give **24** (53 mg, 62%) as a colorless syrup.

2,3,5-Tri-*O*-acetyl-D-arabinofuranose (6). A mixture of glucal **4** (1.28 g, 4.7 mmol), $NaHCO_3$ (40 mg, 0.48 mmol), and dry CH_3OH (0.47 mL) in dry CH_2Cl_2 (15 mL) was treated with ozone at −78 °C until the solution became light blue in color. Dimethyl sulfide (0.69 mL, 9.4 mmol) was added, and the mixture was warmed to room temperature and stirred for 14 h. The mixture was concentrated, redissolved in CH_3OH, and then filtered. The filtrate was concentrated, redissolved in CH_3OH (10 mL) and acetic acid (15 mL), and then stirred at 70 °C for 14 h. The mixture was cooled to room temperature and concentrated to dryness. Purification of the residue by chromatography (hexane/EtOAc, 2:1) gave **6** (935 mg, 72%, 3:2 α/β) as a syrup: R_f 0.48 (hexane/EtOAc, 1:2); partial ^{1}H NMR (300 MHz, $CDCl_3$, δ) 5.55 (d, J = 4.4 Hz, H-1β), 5.40 (s, H-1α); partial ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 100.49 (C-1α), 94.93 (C-1β).

2,3,5-Tri-*O*-acetyl-D-lyxofuranose (7). A mixture of galactal **5** (3.72 g, 13.65 mmol), $NaHCO_3$ (114 mg, 1.36 mmol), and dry CH_3OH (1.4 mL) in dry CH_2Cl_2 (20 mL) at −78 °C was treated as described for the preparation of **6** to give **7** (2.34 g, 62%, 2:1 α/β) as a syrup: R_f 0.41 (hexane/EtOAc, 1:2); partial ^{1}H NMR (300 MHz, $CDCl_3$, δ) 5.45 (d, J = 2.3 Hz, H-1α), 5.43 (d, J = 4.8 Hz, H-1β); partial ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 99.28 (C-1α), 94.77 (C-1β).

1,2,3,5-Tetra-*O*-acetyl-D-arabinofuranose (16). To a stirred solution of triacetate **6** (527 mg, 1.91 mmol) in acetic anhydride (10 mL) at 0 °C was added, dropwise, dilute H_2SO_4 (100 μL of H_2SO_4 dissolved in 1 mL of Ac_2O). After 1 h, the reaction was quenched by adding CH_2Cl_2 and a saturated solution of $NaHCO_3$, and stirring was continued for 10 min. The mixture was diluted with additional CH_2Cl_2 and washed with a saturated solution of $NaHCO_3$, water, and a saturated NaCl solution. The organic layer was dried and filtered, and the filtrate was concentrated in vacuo to give **16** (599 mg, 99%) as a syrup. The ^{1}H NMR spectrum of this compound was identical to that previously reported.[33]

***p*-Cresyl 2,3,5-Tri-*O*-acetyl-1-thio-α-D-arabinofuranoside (17).** Tetraacetate **16** (8.5 g, 25 mmol) was dissolved in dry CH_2Cl_2 (50 mL) and cooled to 0 °C before *p*-thiocresol (3.72 g, 30 mmol) was added. After the mixture was stirred for 20 min under argon, boron trifluoride etherate (17.7 g, 125 mmol) was added via syringe. The mixture was neutralized after 15 min with Et_3N (18 mL, 125 mmol), diluted with CH_2Cl_2, and then washed with water and a saturated NaCl solution. The solution was dried and evaporated, and the crude product was purified by column chromatography (toluene/EtOAc, 4:1) to give **17** (8.4 g, 88%) as a clear syrup: R_f 0.4 (toluene/EtOAc, 4:1); $[\alpha]_D$ +117.6° (*c* 1.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.41−7.35 (d, 2 H), 7.13−7.10 (d, 2 H), 5.47 (d, 1 H, J = 2.3 Hz), 5.26 (t, 1 H, J = 2.3, 2.1 Hz), 5.06 (ddd, 1 H, J = 2.3, 6.6, 0.4 Hz), 4.48 (ddd, 1 H, J = 6.6, 3.7, 5.2 Hz), 4.41 (dd, 1 H, J = 11.9, 3.7 Hz), 4.26 (dd, 1 H, J = 11.9, 5.4 Hz), 2.32 (s, 3 H), 2.17, 2.15, 2.06 (3s, 9 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 170.43, 169.90, 169.48, 138.02, 132.67, 129.7, 91.16, 81.43, 79.92, 77.19, 62.83, 20.72. Anal. Calcd for $C_{18}H_{22}O_7S$: C, 56.53; H, 5.80. Found: C, 56.67; H, 5.78.

1,2,3,5-Tetra-*O*-acetyl-D-lyxofuranose (18). To a solution of triacetate **7** (517 mg, 1.87 mmol) in acetic anhydride (10 mL) at 0 °C was added, dropwise, dilute H_2SO_4 (100 μL of H_2SO_4 dissolved in 1 mL of Ac_2O). After 1 h of stirring, the reaction was worked-up as described for the preparation of **16** to give **18** (590 mg, 99%) as a syrup. The ^{1}H NMR spectrum of this compound was identical to that previously reported.[33]

***p*-Cresyl 2,3,5-Tri-*O*-acetyl-1-thio-α-D-lyxofuranoside (19).** To a solution of tetraacetate **18** (329 mg, 1.03 mmol) in dry CH_2Cl_2 (10 mL) was added *p*-thiocresol (141 mg, 1.14 mmol). The reaction mixture was cooled to 0 °C, and boron trifluoride etherate (157 μL, 1.24 mmol) was added dropwise. After 30 min, Et_3N (0.5 mL) was added, and the reaction was processed as described for the preparation of **17** to give **19** (316 mg, 80%) as a syrup: R_f 0.67 (hexane/EtOAc, 1:1); $[\alpha]_D$ +92° (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.41 (d, 2 H, J = 8.1 Hz), 7.14 (d, 2 H, J = 8.1 Hz), 5.45 (t, 1 H, J = 4.5 Hz), 5.36 (d, 1 H, J = 5.9 Hz), 5.27 (dd, 1 H, J = 4.8, 5.9 Hz), 4.41 (ddd, 1 H, J = 4.3, 5.5, 6.8 Hz), 4.24 (dd, 1 H, J = 5.5, 11.5 Hz), 4.20 (dd, 1 H, J = 6.9, 11.6 Hz), 2.34 (s, 3 H), 2.09 (s, 3 H), 2.06 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 170.39, 169.44, 169.19, 138.48, 133.51, 129.75, 128.06, 87.74, 76.24, 74.76, 70.88, 61.67, 21.04, 20.62, 20.33, 20.29. Anal. Calcd for $C_{18}H_{22}O_7S$: C, 56.54; H, 5.80. Found: C, 56.64; H, 5.82.

Methyl 2,3,5-Tri-*O*-acetyl-α-D-arabinofuranoside (20). Purification by chromatography (hexane/EtOAc, 1:1) gave the product. The ^{1}H NMR spectrum of this compound was identical to that previously reported.[34]

Methyl 2,3,5-Tri-*O*-acetyl-α-D-lyxofuranoside (21). Chromatography (hexane/EtOAc, 3:1 to 2:1) gave the product as a colorless syrup: R_f 0.51 (hexane/EtOAc, 1:1); $[\alpha]_D$ +89° (*c* 1.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 5.57 (t, 1 H, J = 5.5 Hz), 5.21 (dd, 1 H, J = 1.8, 5.1 Hz), 4.98 (d, 1 H, J = 1.8 Hz), 4.47 (ddd, 1 H), 4.25 (dd, 1 H, J = 4.9, 11.7 Hz), 4.19 (dd, 1 H, J = 7.3, 11.6 Hz), 3.40 (s, 3 H), 2.08 (s, 3 H), 2.07 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 170.46, 169.44, 169.27, 105.49, 75.29, 75.21, 71.02, 62.72, 55.44, 20.64, 20.37, 20.25. Anal. Calcd for $C_{12}H_{18}O_8$: C, 49.65; H, 6.25. Found: C, 49.68; H, 6.23.

Octyl 2,3,5-Tri-*O*-acetyl-α-D-arabinofuranoside (22). Purification by chromatography (hexane/EtOAc, 2:1) gave the product as a colorless syrup: R_f 0.57 (hexane/EtOAc, 2:1); $[\alpha]_D$ +60° (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 5.07 (d, 1 H, J = 1.6 Hz), 5.01 (s, 1 H), 4.97 (dd, 1 H, J = 1.4, 4.7 Hz), 4.42 (m, 1 H), 4.22 (m, 2 H), 3.68 (dt, 1 H, J = 6.8, 9.6 Hz), 3.44 (dt, 1 H, J = 6.8, 9.6 Hz), 2.10 (s, 6 H), 2.09 (s, 3 H), 1.58 (m, 2 H), 1.36−1.27 (m, 10 H), 0.88 (t, 3 H, J = 6.9 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 170.41, 169.99, 169.47, 105.41, 81.18, 80.01, 77.11, 67.49, 63.22, 31.64, 29.22, 29.13, 29.08, 25.85, 22.48, 20.59, 20.55, 13.90. Anal. Calcd for $C_{19}H_{32}O_8$: C, 58.75; H, 8.30. Found: C, 58.70; H, 8.21.

Methyl 6-*O*-(2,3,5-Tri-*O*-acetyl-α-D-arabinofuranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (23). Chromatography (hexane/EtOAc, 1:1) gave the product as a colorless syrup: R_f 0.52 (hexane/EtOAc, 1:1); $[\alpha]_D$ +50° (*c* 1.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.26−7.36 (m, 15 H), 5.14 (m, 2 H), 4.99 (d, 1 H, J = 10.8 Hz), 4.96 (dd, 1 H, J = 1.4, 4.6 Hz), 4.89 (d, 1 H, J = 10.8 Hz), 4.81 (d, 1 H, J = 10.9 Hz), 4.80 (d, 1 H, J = 12.1 Hz), 4.67 (d, 1 H, J = 12.4 Hz), 4.63 (d, 1 H, J = 11.1 Hz), 4.60 (d, 1 H, J = 3.7 Hz), 4.34 (dd, 1 H, J = 3.0, 11.2 Hz), 4.20 (m, 1 H), 4.14 (dd, 1 H, J = 5.7, 11.3 Hz), 4.0 (dd, 1 H, J = 3.6, 11.2 Hz), 3.9 (t, 1 H, J = 9.4 Hz), 3.75 (ddd, 1 H, J = 1.7, 3.6, 9.9 Hz), 3.68 (dd, 1 H, J = 1.7, 11.1 Hz), 3.59 (t, 1 H, J = 9.0 Hz), 3.55 (dd, 1 H, J = 3.5, 9.6 Hz), 3.37 (s, 3 H), 2.08 (s, 3 H), 2.02 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 170.45, 169.91, 169.29, 138.64, 138.14, 138.04, 128.37, 128.30, 128.02, 127.86, 127.81, 127.71, 127.57, 127.52, 105.88, 97.98, 81.88, 80.99, 80.53, 79.84, 77.59, 77.05, 75.65, 74.85, 73.29, 69.67, 65.91, 63.18, 55.04, 20.63, 20.61. Anal. Calcd for $C_{39}H_{46}O_{13}$: C, 64.81; H, 6.41. Found: C, 64.64; H, 6.35.

Methyl 6-*O*-(2,3,5-Tri-*O*-acetyl-α-D-lyxofuranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (24). Chromatography (hexane/EtOAc, 3:1 to 1:1) gave the product as a syrup: R_f 0.46 (hexane/EtOAc, 1:1); $[\alpha]_D$ +62° (*c* 1.4, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.35−7.26 (m, 15 H), 5.57 (t, 1 H, J = 5.6 Hz), 5.26 (dd, 1 H, J = 1.7, 5.1 Hz), 5.17 (d, 1 H, J = 1.7 Hz), 4.99 (d, 1 H, J = 10.9 Hz), 4.89 (d, 1 H, J = 10.7 Hz), 4.82 (d, 1 H, J = 10.9 Hz), 4.80 (d, 1 H, J = 12.1 Hz), 4.66 (d, 1 H, J = 12.1 Hz), 4.61 (d, 1 H, J = 10.4 Hz), 4.58 (d, 1 H, J = 3.2

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Hz), 4.43 (ddd, 1 H, J = 4.7, 5.9, 7.4 Hz), 4.20 (dd, 1 H, J = 4.7, 11.7 Hz), 4.12 (dd, 1 H, J = 7.4, 11.7 Hz), 4.02−3.95 (m, 2 H), 3.75−3.66 (m, 2 H), 3.55−3.49 (m, 2 H), 3.36 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 1.96 (s, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 170.46, 169.41, 169.18, 138.64, 138.11, 138.04, 128.37, 128.34, 128.30, 127.08, 127.82, 127.76, 127.69, 127.49, 104.71, 98.02, 81.88, 79.79, 77.42, 75.63, 75.38, 74.94, 73.35, 70.96, 69.71, 66.52, 62.80, 55.10, 20.57, 20.44, 20.31. Anal. Calcd for $C_{39}H_{46}O_{13}$: C, 64.81; H, 6.41. Found: C, 64.56; H, 6.39.

Methyl 5-*O*-(2,3,5-Tri-*O*-acetyl-α-D-arabinofuranosyl)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (25). Chromatography (toluene/EtOAc, 9:1) yielded the product as a clear syrup: R_f 0.18 (toluene/EtOAc, 9:1); $[\alpha]_D$ +19.2° (*c* 3.7, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.11−7.26 (m, 10 H), 5.61 (d, 1 H, J = 4.8 Hz), 5.49 (s, 1 H), 5.22 (s, 1 H), 5.21 (s, 1 H), 5.14 (s, 1 H), 4.94 (d, 1 H, J = 4.5 Hz), 4.48−4.33 (m, 3 H), 4.22 (dd, 1 H, J = 5.4, 11.4 Hz), 4.12 (dd, 1 H, J = 3.3, 10.5 Hz), 3.85 (d, 1 H, J = 12 Hz), 3.47 (s, 3 H), 2.09, 2.07, 1.87 (3s, 9 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 170.61, 170.31, 169.41, 165.72, 165.49, 133.60, 133.48, 129.94, 129.90, 129.28, 129.22, 128.60, 128.50, 106.83, 105.45, 82.19, 81.49, 81.14, 80.90, 77.37, 76.99, 65.42, 63.31, 54.92, 20.80, 20.76, 20.47. Anal. Calcd $C_{31}H_{34}O_{14}$: C, 57.40; H, 5.61. Found: C, 57.74; H, 5.49.

Methyl 5-*O*-(2,3,5-Tri-*O*-acetyl-α-D-lyxofuranosyl)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (26). Chromatography (hexane/EtOAc, 1:1) gave the product as a syrup: R_f 0.44 (hexane/EtOAc, 1:1); $[\alpha]_D$ +26° (*c* 1.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.07−7.40 (m, 10 H), 5.57 (t, 1 H, J = 5.6 Hz), 5.45 (m, 2 H), 5.31 (dd, 1 H, J = 1.5, 5.2 Hz), 5.21 (d, 1 H, J = 1.2 Hz), 5.13 (s, 1 H), 4.53 (m, 1 H), 4.37 (m, 1 H), 4.23 (dd, 1 H, J = 4.9, 11.7 Hz), 4.19 (dd, 1 H, J = 4.4, 11.8 Hz), 4.11 (dd, 1 H, J = 4.8, 11.1 Hz), 3.90 (dd, 1 H, J = 3.2, 11.2 Hz), 3.47 (s, 3 H), 2.05 (s, 6 H), 2.03 (s, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 170.48, 169.30, 169.16, 165.60, 165.35, 133.44, 133.35, 129.80, 129.72, 129.11, 128.99, 128.50, 128.36, 106.76, 104.69, 81.95, 81.35, 77.37, 75.46, 75.42, 70.94, 66.93, 62.63, 54.88, 20.65, 20.38, 20.26. Anal. Calcd for $C_{31}H_{34}O_{14}\cdot H_2O$: C, 57.41; H, 5.59. Found: C, 57.13; H, 5.24.

Octyl 5-*O*-(2,3,5-Tri-*O*-acetyl-α-D-lyxofuranosyl)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (27). Chromatography (hexane/EtOAc, 1:1) gave the product as a colorless syrup: R_f 0.71 (hexane/EtOAc, 1:1); $[\alpha]_D$ +83° (*c* 1.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.36−7.26 (m, 10 H), 5.54 (t, 1 H, J = 5.6 Hz), 5.25 (dd, 1 H, J = 1.7, 5.1 Hz), 5.13 (d, 1 H, J = 1.6 Hz), 5.01 (d, 1 H, J = 1.0 Hz), 4.59 (d, 2 H, J = 11.9 Hz), 4.50 (d, 1 H, J = 11.9 Hz), 4.49 (d, 1 H, J = 11.9 Hz), 4.41 (ddd, 1 H, J = 4.8, 6.0, 7.3 Hz), 4.21 (dd, 1 H, J = 4.7, 11.7 Hz), 4.15 (dd, 1 H, J = 7.4, 11.5 Hz), 4.13 (ddd, 1 H, J = 3.5, 4.6, 7.1 Hz), 4.01 (dd, 1 H, J = 1.4, 3.5 Hz), 3.88 (dd, 1 H, J = 3.4, 6.9 Hz), 3.83 (dd, 1 H, J = 4.8, 11.2 Hz), 3.70 (dt, 1 H, J = 6.7, 9.6 Hz), 3.66 (dd, 1 H, J = 3.5, 11.2 Hz), 3.38 (dt, 1 H J = 6.6, 9.6 Hz), 2.06 (s, 3 H), 2.05 (s, 6 H), 1.61−1.55 (m, 2 H), 1.33−1.27 (m, 10 H), 0.88 (t, 3 H, J = 6.9 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 170.49, 169.38, 169.18, 137.74, 137.46, 128.33, 128.29, 127.83, 127.75, 127.67, 105.98, 104.62, 88.16, 83.14, 79.7, 75.30, 75.24, 72.06, 71.90, 70.98, 67.65, 67.20, 62.78, 31.73, 29.41, 29.27, 29.17, 26.02, 22.55, 20.68, 20.40, 20.29, 14.00. Anal. Calcd for $C_{38}H_{52}O_{12}$: C, 65.13; H, 7.48. Found: C, 64.96; H, 7.44.

Methyl 3-*O*-(2,3,5-Tri-*O*-acetyl-α-D-arabinofuranosyl)-5-*O*-*tert*-butyldiphenylsilyl-2-*O*-benzoyl-α-D-arabinofuranoside (28). Chromatography (hexane/EtOAc, 9:1) gave **11** (477 mg, 79%) as a syrup: R_f 0.35 (hexane/EtOAc, 6:1); $[\alpha]_D$ +20.3° (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.99−7.97 (m, 2 H), 7.70−7.53 (m, 4 H), 7.42−7.26 (m, 7 H), 5.40 (s, 1 H), 5.30 (d, 1 H, J = 1.2 Hz), 5.18 (d, 1 H, J = 1.6 Hz), 5.09 (s, 1 H), 4.97 (dd, 1 H, J = 1.6, 5.1 Hz), 4.46 (m, 1 H), 4.26−4.04 (m, 4 H), 3.89−3.87 (m, 2 H), 3.44 (s, 3 H), 2.10 (s, 3 H), 2.08 (s, 3 H), 1.96 (s, 3 H), 1.03 (s, 9 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 170.49, 170.01, 169.48, 165.59, 135.64, 135.59, 133.36, 133.29, 129.87, 129.77, 129.70, 129.34, 128.39, 127.72, 127.66, 127.27, 107.14, 104.81, 84.94, 83.21, 82.60, 81.19, 80.47, 79.97, 77.22, 63.05, 62.94, 54.74, 26.74, 20.75, 19.33. Anal. Calcd for $C_{40}H_{48}O_{13}Si$: C, 62.81; H, 6.32. Found: C, 62.94; H, 6.46.

Methyl 3-*O*-(2,3,5-Tri-*O*-acetyl-α-D-lyxofuranosyl)-5-*O*-*tert*-butyldiphenylsilyl-2-*O*-benzoyl-α-D-arabinofuranoside (29). Purification by chromatography (hexane/EtOAc, 2:1) gave the product as a colorless syrup: R_f 0.41 (hexane/EtOAc, 2:1); $[\alpha]_D$ +62.0° (*c* 1.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.99 (m, 2 H), 7.70 (m, 4 H), 7.57 (m, 1 H), 7.43−7.32 (m, 8 H), 5.56 (t, 1 H, J = 5.5 Hz), 5.43 (d, 1 H, J = 1.6 Hz), 5.30 (dd, 1 H, J = 1.7, 5.2 Hz), 5.24 (d, 1 H, J = 1.2 Hz), 5.09 (s, 1 H), 4.39 (m, 1 H), 4.24−4.11 (m, 3 H), 4.03 (dd, 1 H, J = 7.3, 11.5 Hz), 3.94 (dd, 1 H, J = 4.7, 11.3 Hz), 3.87 (dd, 1 H, J = 3.6, 11.3 Hz), 3.44 (s, 3 H), 2.09 (s, 3 H), 2.07 (s, 3 H), 1.90 (s, 3 H), 1.03 (s, 9 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 170.33, 169.36, 169.20, 165.49, 135.54, 135.49, 133.26, 133.23, 129.74, 129.60, 129.57, 129.20, 128.28, 127.59, 127.54, 106.84, 103.77, 83.26, 82.63, 80.80, 75.40, 75.33, 70.79, 62.91, 62.50, 54.53, 26.62, 20.48, 20.39, 20.27, 19.20. Anal. Calcd for $C_{40}H_{48}O_{12}Si\cdot 0.5H_2O$: C, 62.07; H, 6.31. Found: C, 62.13; H, 6.21.

Methyl α-D-Arabinofuranosyl-(1→5)-α-D-arabinofuranoside (30). Disaccharide **25** (160 mg, 0.25 mmol) dissolved in dry CH_3OH (5 mL) was treated with a catalytic amount of sodium methoxide. The mixture was stirred for 4 h and then neutralized with prewashed Amberlite IR-118 (H+) resin. The solution was filtered, and the resulting residue was taken up in CH_2Cl_2. The product was extracted into water, and the water layer was concentrated. Purification by column chromatography ($CHCl_3/CH_3OH$, 3:1) yielded **30** (67 mg, 90%) as a clear syrup: $[\alpha]_D$ −157° (*c* 1.6, H_2O); R_f 0.7 ($CHCl_3/CH_3OH$, 2:1); ^{1}H NMR (600 MHz, D_2O, δ) 4.99 (d, 1 H, J = 1.5 Hz, H-1′), 4.85 (d, 1 H, J = 1.5 Hz, H-1), 4.08 (ddd, 1 H, J = 5.5, 3.4, 5.8 Hz, H-4), 4.04 (dd, 1 H, J = 1.3, 3.1 Hz, H-2′), 4.01 (ddd, 1 H, J = 5.5, 3.4, 6.1 Hz, H-4′), 3.98 (dd, 1 H, J = 1.5, 3.1 Hz, H-2), 3.92 (dd, 1 H, J = 3.1, 5.8 Hz, H-3), 3.87 (dd, 1 H, J = 3.1, 6.1 Hz, H-3′), 3.80 (dd, 1 H, J = 5.5, 11.3 Hz, H-5*R*), 3.74 (dd, 1 H, J = 3.4, 12.5 Hz, H-5′*S*), 3.72 (dd, 1 H, J = 3.4, 11.3 Hz, H-5*S*), 3.63 (dd, 1 H, J = 5.5, 12.5 Hz, H-5′*R*), 3.34 (s, 3 H, OCH_3); ^{13}C NMR (125 MHz, D_2O, δ) 109.31 (C-1), 108.31 (C-1′), 84.87 (C-4′), 83.14 (C-4), 81.79 (C-2′), 81.49 (C-2′), 77.46 (C-3), 77.43 (C-3′), 67.73 (C-5), 62.08 (C-5′), 55.88 (OCH_3) HR−FABMS *m*/*z* calcd for $[C_{11}H_{20}O_9]H^+$ 297.1185, found 297.1174.

Methyl α-D-Lyxofuranosyl-(1→5)-α-D-arabinofuranoside (31). Disaccharide **18** (55 mg, 0.09 mmol) was dissolved in dry CH_3OH (5 mL), and then 0.1 M methanolic $NaOCH_3$ (0.5 mL) was added dropwise. After 4 h, the reaction mixture was neutralized with Amberlite IR-118 (H^+) resin, filtered, and evaporated, and the residue was chromatographed ($CHCl_3/CH_3OH$, 2:1) to give **31** (18 mg 69%) as a syrup: R_f 0.56 ($CHCl_3/CH_3OH$, 2:1); $[\alpha]_D$ +136° (*c* 1.1, H_2O); ^{1}H NMR (300 MHz, D_2O, δ) 4.97 (d, 1 H, J = 3.2 Hz, H-1′), 4.80 (d, 1 H, J = 1.1 Hz, H-1), 4.26 (t, 1 H, J = 4.6 Hz, H-3′), 4.17 (td, 1 H, J = 4.3, 6.6 Hz, H-4′), 4.05 (dd, 1 H, J = 3.3, 4.8 Hz, H-2′), 4.01 (dt, 1 H, J = 3.4, 5.7 Hz, H-4), 3.93 (dd, 1 H, J = 1.7, 3.3 Hz, H-2), 3.85 (dd, 1 H, J 3.3, 5.8 Hz, H-3), 3.75 (dd, 1 H, J = 5.6, 11.4 Hz, H-5*R*), 3.71 (dd, 1 H, J = 4.2, 11.9 Hz, H-5′*S*), 3.67 (dd, 1 H, J = 3.1, 10.9 Hz, H-5*S*), 3.62 (dd, 1 H, J = 6.6, 11.9 Hz, H-5′*R*), 3.28 (s, 3 H, OCH_3); ^{13}C NMR (75.5 MHz, D_2O, δ) 108.38 (C-1), 107.13 (C-1′), 82.21 (C-4), 80.69 (C-2), 80.39 (C-4′), 76.54 (C-3), 75.95 (C-2′), 71.03 (C-3′), 67.59 (C-5), 60.19 (C-5′), 55.03 (OCH_3). HR−FABMS *m*/*z* calcd for $[C_{11}H_{20}O_9]Na^+$ 319.1005, found 319.0996.

Octyl α-D-Lyxofuranosyl-(1→5)-α-D-arabinofuranoside (32). A solution of **21** (66 mg, 0.09 mmol) in dry CH_3OH (5 mL) was hydrogenated over 10% Pd/C (25 mg) under a flow of H_2 for 4 h. The catalyst was filtered off, and the filtrate was concentrated. A solution of the residue in dry CH_3OH (5 mL) was stirred with 0.1 M methanolic sodium methoxide (0.5 mL) for 2 h. Neutralization with prewashed Amberlite IR-118 (H^+) resin followed by filtration and concentration gave a residue that was purified by chromatography ($CHCl_3/CH_3OH$, 3:1) to yield **32** (31 mg, 84%) as a syrup: R_f 0.73 ($CHCl_3/CH_3OH$, 3:1); $[\alpha]_D$ +85° (*c* 1.0, H_2O); ^{1}H NMR (300 MHz, D_2O, δ) 4.95 (d, 1 H, J = 2.8 Hz, H-1′), 4.82 (d, 1 H, J = 1.6 Hz, H-1), 4.29 (t, 1

H, J = 4.8 Hz, H-3′), 4.15 (td, 1 H, J = 4.4, 6.1 Hz, H-4′), 4.04 (dd, 1 H, J = 2.8, 4.9 Hz, H-2′), 3.97 (m, 1 H, H-4), 3.93 (dd, 1 H, J = 1.6, 3.8 Hz, H-2), 3.87 (dd, 1 H, J = 3.7, 6.5 Hz, H-3), 3.76 (dd, 1 H, J = 4.6, 11.3 Hz, H-5*S*), 3.71 (dd, 1 H, J = 4.2, 11.8 Hz, H-5′*S*), 3.66−3.55 (m, 3 H, H-5*R*, 5′*R*, OCH_2), 3.34 (dt, 1 H, J = 6.8, 9.2 Hz, OCH_2), 1.48 (m, 2 H, OCH_2CH_2), 1.18 (m, 10 H, octyl CH_2), 0.76 (t, 3 H, J = 6.8 Hz, octyl CH_3); ^{13}C NMR (75.5 MHz, D_2O, δ) 107.41 (C-1), 107.15 (C-1′), 81.74 (C-4), 81.47 (C-2), 80.18 (C-4′), 76.81 (C-3), 75.82 (C-2′), 71.02 (C-3′), 68.26 (C-5), 67.10 (octyl C1), 60.17 (C-5′), 31.84 (octyl C2), 29.39, 29.27, 25.94, 22.60 (octyl C3−C7), 13.82 (octyl CH_3). HR−FABMS m/z calcd for $[C_{18}H_{34}O_9]Na^+$ 417.2105, found 417.2104.

Methyl α-D-Arabinofuranosyl-(1→3)-α-D-arabinofuranoside (33). A solution of disaccharide **28** (300 mg, 0.39 mmol) dissolved in dry THF (3 mL) was cooled to 0 °C and then treated with TBAF (0.5 mL, 1 M solution in THF). After 1 h, the reaction mixture was taken up in CH_2Cl_2, and the organic layer was washed with aqueous solutions of ammonium sulfate and saturated NaCl before being dried and concentrated. The mixture was taken up in CH_3OH (5 mL) and treated with a catalytic amount of sodium methoxide for 1 h. The mixture was then neutralized with Amberlite IR-118 (H^+) resin, filtered, evaporated, and purified by chromatography ($CHCl_3/CH_3OH$, 3:1) to yield **33** (93 mg, 81%) as a clear syrup: R_f 0.33 ($CHCl_3/CH_3OH$, 3:1); $[\alpha]_D$ +148.3° (*c* 0.9, H_2O); ^{1}H NMR (600 MHz, D_2O, δ) 5.07 (d, 1 H, J = 1.6 Hz, H-1′), 4.88 (d, 1 H, J = 1.2 Hz, H-1), 4.29 (dd, 1 H, J = 1.3, 2.0 Hz, H-2), 4.06 (ddd, 1 H, J = 5.5, 3.4, 5.8 Hz, H-4), 4.03 (dd, 1 H, J = 1.6, 3.4 Hz, H-2′), 3.95−3.99 (m, 2 H, H-3, H-4), 3.86 (dd, 1 H, J = 3.4, 6.2 Hz, H-3′), 3.78 (dd, 1 H, J = 3.4, 12.5 Hz, H-5*S*), 3.72 (dd, 1 H, J = 3.4, 12.1 Hz, H-5′*S*), 3.68 (dd, 1 H, J = 5.8, 12.5 Hz, H-5*R*), 3.63 (dd, 1 H, J = 5.8, 12.1 Hz, H-5′*R*), 3.34 (s, 3 H, OCH_3); ^{13}C NMR (125 MHz, D_2O, δ) 109.34 (C-1), 107.94 (C-1′), 84.77 (C-4′), 84.02 (C-4), 82.98 (C-3), 82.04 (C-2′), 79.96 (C-2), 77.43 (C-3′), 62.03 (C-5), 61.95 (C-5′), 55.65 (OCH_3). HR−FABMS m/z calcd for $[C_{11}H_{20}O_9]Na^+$ 319.1005, found 319.1012.

Methyl α-D-Lyxofuranosyl-(1→3)-α-D-arabinofuranoside (34). A solution of **29** (79 mg, 0.11 mmol) in dry THF (5 mL) at 0 °C was stirred with TBAF (1.0 M solution in THF, 0.5 mL). After 3 h, the solvent was removed under reduced pressure. The residue was dissolved in dry CH_3OH (3 mL) and treated with 0.1 M sodium methoxide (0.5 mL) for 2 h at room temperature. The pH of the solution was adjusted to 7.0 by addition of Amberlite IR-118 (H^+) resin, and the filtrate obtained upon removal of the resin was evaporated to dryness. Chromatography of the residue ($CHCl_3/CH_3OH$, 2:1) gave **34** (24 mg, 77%) as a syrup: R_f 0.24 ($CHCl_3/CH_3OH$, 2:1); $[\alpha]_D$ +103.0° (*c* 0.8, H_2O); ^{1}H NMR (300 MHz, D_2O, δ) 4.99 (d, 1 H, J = 3.1 Hz, H-1′), 4.77 (s, 1 H, H-1), 4.19 (t, 1 H, J = 4.6 Hz, H-3′), 4.07 (td, 1 H, J = 4.1, 6.8 Hz, H-4′), 4.02 (dd, 1 H, J = 1.1, 2.1 Hz, H-2), 3.98 (dd, 1 H, J = 3.2, 4.9 Hz, H-2′), 3.93 (dt, 1 H, J = 3.4, 5.6 Hz, H-4), 3.82 (dd, 1 H, J = 1.8, 5.2 Hz, H-3), 3.68 (dd, 1 H, J = 3.4, 12.2 Hz, H-5*S*), 3.65 (dd, 1 H, J = 4.3, 12.0 Hz, H-5′*S*), 3.57 (dd, 1 H, J = 5.8, 12.3 Hz, H-5*R*), 3.56 (dd, 1 H, J = 6.6, 12.3 Hz, H-5′*R*), 3.23 (s, 3 H, OCH_3); ^{13}C NMR (75.5 MHz, D_2O, δ) 108.41 (C-1), 106.76 (C-1′), 83.32 (C-4), 82.72 (C-3), 80.41 (C-4′), 79.05 (C-2), 76.04 (C-2′), 70.96 (C-3′), 61.03 (C-5), 60.16 (C-5′), 54.71 (OCH_3). HR−FABMS m/z calcd for $[C_{11}H_{20}O_9]Na^+$ 319.1005, found 319.1028.

***p*-Cresyl 2,3,5-Tri-*O*-acetyl-1-thio-α-D-[U-$^{13}C_5$]-arabinofuranoside (38).** The chromatographic properties of this compound were identical to those of its unlabeled parent **17**: ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 91.04 (dt, J = 2.6, 41.1 Hz), 81.31 (t, J = 43.2 Hz), 79.81 (ddd, J = 3.1, 39.6, 43.4 Hz), 77.01 (ddd, J = 1.8, 39.5, 41.4 Hz), 62.70 (d, J = 44.3 Hz).

Methyl 2,3,5-Tri-*O*-acetyl-α-D-[U-$^{13}C_5$]-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (39). The chromatographic properties of this compound were identical to those of its unlabeled parent **25**: ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 170.50, 170.20, 169.29, 165.58, 165.36, 133.49, 133.36, 129.80, 129.77, 129.13, 129.06, 128.47, 128.36, 106.60, 105.28 (d, J = 48.6 Hz), 82.04, 81.36, 81.01 (ddd, J = 1.8, 37.1, 42.8 Hz), 80.75 (t, J = 46.9 Hz), 77.06 (dd, J = 39.3, 44.4 Hz), 76.83, 65.21, 63.17 (d, J = 44.7), 65.21, 63.17 (d, J = 44.7 Hz), 54.80, 20.68, 20.64, 20.35.

Methyl [U-$^{13}C_5$]-Arabinofuranosyl-(1→5)-α-D-arabinofuranoside (40). The chromatographic properties of this compound were identical to those of its unlabeled parent **30**: ^{13}C NMR (75.5 MHz, D_2O, δ) 108.47, 107.46 (d, J = 47.3 Hz), 84.01 (ddd, J = 3.0, 39.2, 42.2 Hz), 82.32 (d, J = 2.2 Hz), 80.94 (dd, J = 40.8, 46.8 Hz), 80.64, 76.56, 76.52 (t, J = 39.2 Hz), 66.90, 61.21 (d, J = 42.4 Hz), 55.04. HR−FABMS calcd for $[^{12}C_6{}^{13}C_5H_{20}O_9]Na^+$ 324.1173, found 324.1219.

Acknowledgment. This work was supported by The Ohio State University and the NSF REU (P.E.C.) and GAANN (J.D.A.) programs. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We thank Dr. Charles Cottrell for the high-field NMR spectra.

Supporting Information Available: ^{1}H and ^{13}C spectra for compounds **26**, **29**−**34**, and **40** (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

JO9815406