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Wittig reaction of unprotected D-aldopentoses with stabilized ylides: metal-ion effects

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ABSTRACT

Each of the four D-aldopentoses (**1–4**) reacts in the unprotected form with Ph_3PCHCO_2Me (**5**) in THF to give stereoselectively the coresponding *trans*-α,β-unsaturated C_7 Wittig adducts, isolated as the corresponding 4,5,6,7-tetraacetates (**7–10**) or 4,5:6,7-di-*O*-isopropylidene derivatives (**11–14**). Concurrently formed are also bicyclic, 1,4-lactone derivatives, isolated as their 5,7-diacetates (**15–18**) or 5,7-*O*-isopropylidene derivatives (**19**), arising through intramolecular Michael addition from the initial acyclic adducts. Formation of the cyclized products is suppressed by incorporation of $Cu(OAc)_2$ in the reaction mixture, permitting preparative isolation of the hept-3-enonate derivatives **7–10**, useful as dienophiles in Diels–Alder carbocyclizations with chirality transfer. Optimized yields were 25% (D-*ribo*), 50% (D-*arabino*), 49% (D-*xylo*), and 61% (D-*lyxo*). Under $Cu(OAc)_2$-catalyzed conditions, the formation of small proportions of 3,7-anhydroheptonic acid esters (**21** and **23**) was observed in the D-*arabino* and D-*xylo* series, but not with the other two pentoses.

INTRODUCTION

The Wittig reaction is one of the most versatile procedures for the controlled introduction of a carbon–carbon double bond from a carbonyl precursor. This reaction has found significant use in the carbohydrate field[1] as a route to higher-carbon sugar derivatives through subsequent osmylation[2] or epoxidation, followed by ring-opening[3] reactions. These subsequent reactions, as well as cycloaddition reactions, are double-centered processes involving both carbon atoms of the alkene, and are generally stereospecific[4], with the stereochemical outcome depending on the *E* or *Z* configuration of the starting alkene.

In connection with our studies on stereocontrol in Diels–Alder cycloaddition reactions[5–8] employing the chiral pool furnished by abundant sugars, we required various examples of enantiomerically pure, unsaturated acyclic-sugar derivatives accessible through two-carbon chain extension from aldopentose precursors. In

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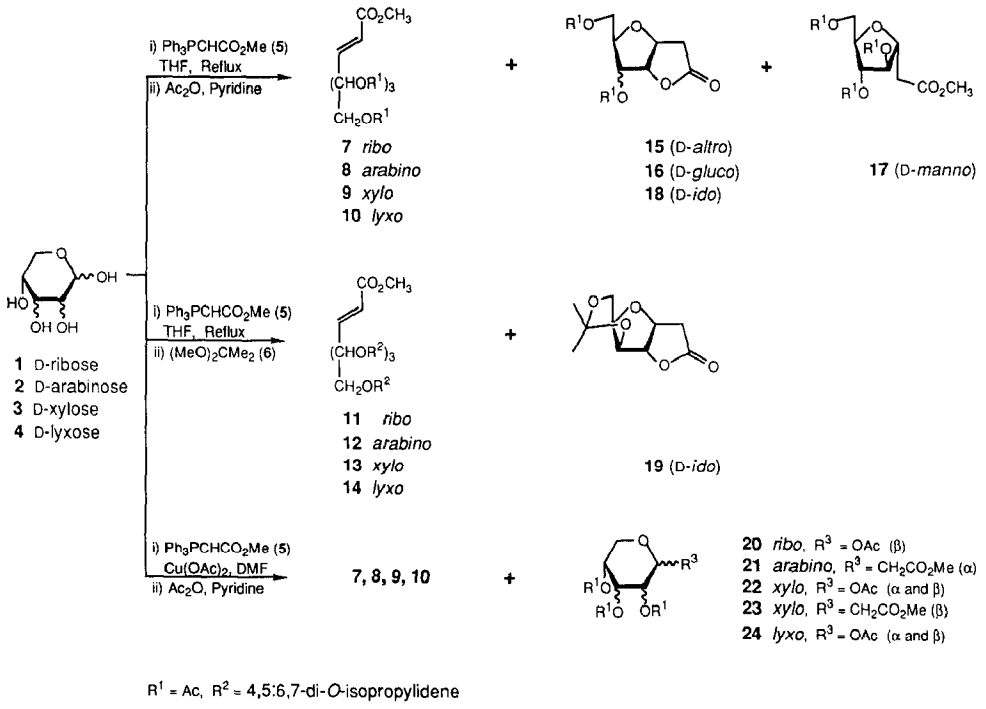
consequence, it is important to have convenient preparative access to the acyclic unsaturated-sugar derivatives in a stereoselective manner, or as readily separable *E*,*Z* isomers.

Conventional methods[7] for preparing 2,3-unsaturated cyclic sugars by the Wittig route require several steps: conversion of the aldose precursor into the acyclic form as the dithioacetal, protection of the chain through acylation, deprotection of the carbonyl group, and finally reaction with the appropriate ylide. However, a recent review on the Wittig alkenation reaction[9] documents several examples of γ- and δ-hydroxyaldehydes that exist predominantly as cyclic hemiacetals but which nevertheless participate well in Wittig reactions, especially with stabilized ylides. The α,β-unsaturated alkenes initially formed may be isolated under carefully controlled conditions, but are prone to cyclization by intramolecular Michael addition. This cyclization may be minimized by incorporating benzoic acid in the reaction medium[10] or using a bulky group (*tert*-butyl ester) in the ylide[11]. However, minor variations in the reaction conditions (solvent, temperature) or use of different ylides led to either alkenes[12] or cyclized *C*-glycosyl compounds[13], even with the same starting lactol (2,3-*O*-isopropylidene-D-ribose). Neither the factors influencing the stereochemistry of the alkene nor the relationship between alkene stereochemistry and the stereochemistry of *C*-glycosyl products resulting from subsequent Michael addition are well understood, even though various types of partially protected lactols have been used to investigate the scope of the Wittig reaction and the Wittig–Michael cyclization sequence. Furthermore, several steps of chemical modification (anomeric protection, protection of other hydroxyl groups, anomeric deprotection) are required to obtain the partially protected lactols from the starting sugars.

Our purpose in this present work was to simplify the steps required to prepare the desired acyclic-sugar enonates, either stereoselectively or as readily separable *E*,*Z* mixtures, from readily available unprotected sugars. The literature already records[1] the direct reaction of D-ribose and D-xylose with stabilized ylides but, as might be expected, complex mixtures of products are formed as a result of intramolecular Michael-addition to the α,β-unsaturated products as soon as they are formed. For successful use of this direct approach, modifications to suppress this 1,4-addition process are required. Here we describe convenient preparative conditions for one-step conversion of each of the D-aldopentoses (**1**–**4**) into the seven-carbon *trans*-2,3-unsaturated derivatives through direct reaction with methyl (triphenylphosphoranylidene)acetate (**5**), and the use of metal-ion effects to diminish intramolecular cyclization as a competing reaction.

RESULTS AND DISCUSSION

Wittig reaction of unprotected D-*aldopentoses.*—*With* D-*ribose* (**1**). Wittig condensation of unprotected D-ribose (**1**) with stabilized ylide **5** in boiling THF, followed by conventional acetylation of the mixture with acetic anhydride–pyridine gave,



Scheme 1.

after chromatographic resolution, a 25% yield of methyl (*E*)-4,5,6,7-tetra-*O*-acetyl-2,3-dideoxy-D-*ribo*-hept-2-enonate (**7**) as a syrup, $[\alpha]_D + 18°$, along with 57% of 5,7-di-*O*-acetyl-3,6-anhydro-2-deoxy-D-*altro*-heptono-1,4-lactone (**15**), also a syrup, $[\alpha]_D + 185°$.

The ^{1}H NMR spectrum of the acyclic alkene **7** revealed two alkenic protons that were *trans*-related ($J_{2,3}$ 15.7 Hz), and no *cis* alkenic protons were present. The intramolecular Michael-addition product was assigned as the [3.3.0]bicyclo product **15**, rather than a possible [4.3.0]bicyclo product **25**, from its ^{1}H NMR spectrum. The small $J_{6,7}$ coupling constant (4.9 Hz) might have confirmed that product was not the [4.3.0]bicyclo isomer **25**, which would have had $J_{6,7} > 8$ Hz because of the *trans* diaxial disposition of two protons in the pyranoside ring. However a rapid equilibrium between the two chair confomers (**25A** and **25B**, Fig. 1) of **25** could lead to a small $J_{6,7}$ value. This ambiguity was resolved by considering the large $J_{5,6}$ value (8.3 Hz), which eliminates the possibility of structure **25**. Neither **25A** nor **25B** would show such a large coupling constant because both have the axial–equatorial disposition of H-5 and H-6 in a six-membered ring. Another plausible formulation of the cyclized product, a [3.2.1]bicyclic 1,5-lactone (**26**) an analogue of which was formed in the Wittig reaction of D-galactose[14], was eliminated by considering the ^{1}H NMR and IR spectra of **15**. It is well established[15] that α-hydrogens of 1,5-lactones exhibit a greater downfield

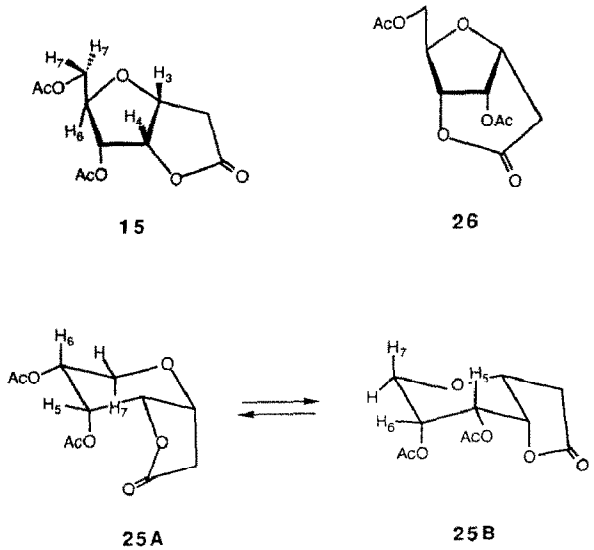
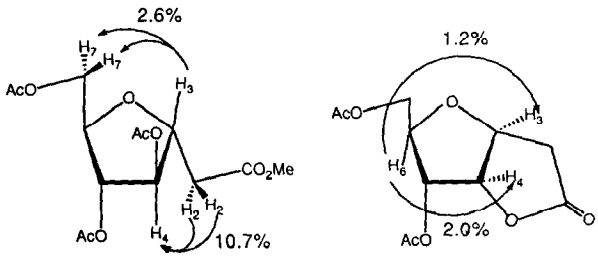


Fig. 1. Possible isomers of the cyclized product from the Wittig reaction on D-ribose.

chemical-shift (δ 3.3) than those of 1,4-lactones (δ 2.2–2.5). The two α-hydrogens of **15**, however, show intermediate chemical shifts δ 2.69, 2.80. The IR spectrum of the product showed the C=O stretching band at 1780 cm^{-1}. As 1,5-lactones generally have a C=O stretching band at relatively small wavenumbers[16], (1735 cm^{-1}), the cyclized compound may thus be formulated as the 1,4-lactone **15**, rather than the 1,5-lactone **26**.

When the mixture from direct Wittig reaction with D-ribose was treated with 2,2-dimethoxypropane (**6**) in the presence of acid at elevated temperature (90°), one major nonpolar product (R_f 0.72, 1:2 EtOAc–hexanes) was obtained as a syrup in 29% yield after chromatographic resolution, $[\alpha]_D$ −35.2° in chloroform, and was formulated as the 4,5:6,7-di-*O*-isopropylidene analogue (**11**) of compound **7**. The ^1H NMR spectrum of **11** showed that it was desired *trans* unsaturated sugar ($J_{2,3}$ 15.5 Hz) and no *cis* alkene protons were observed.

With D-*arabinose* (**2**). The same Wittig condensation was next performed with D-arabinose in boiling THF, with subsequent acetylation. Three major products (R_f 0.52, 0.4, and 0.19, 1:1 EtOAc–hexanes) were formed and were separated by flash chromatography. The fastest moving spot was the crystalline *E*-unsaturated sugar 8 (26%), which had the same mp (116°C, lit.[7] 116–117°C) and spectral data as the compound prepared[7] previously from *aldehydo*-D-arabinose tetraacetate. The spot of intermediate mobility was identified as the *C*-furanosyl derivative **17**, produced in 25% yield, $[\alpha]_D$ + 15.7° (*c* 0.75, CH_2Cl_2). It showed three methyl peaks for acetyl groups (δ 2.05, 2.06 double intensity), and a methoxyl peak (δ 3.66) in its ^1H NMR spectrum, indicating that it was not a lactonized product. The relative configuration at C-3 was assigned as α-*C*-glycofuranosyl (D-*manno*) by an NOE experiment (benzene-d_6). When the protons at C-2, (H-2 and H-2′), were



17 16

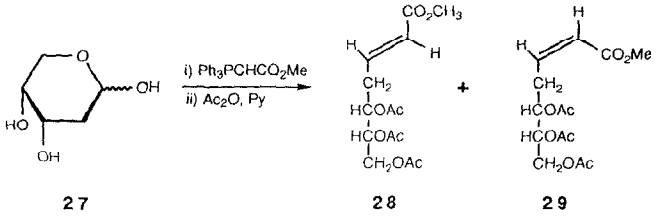
Fig. 2. NOE enhancement of compounds **17** and **16**.

irradiated, a large NOE enhancement (10.7%) occurred at H-4 (Fig. 2). In addition, H-5, H-7, and H-7′ were affected by 1.6 and 2.6%, respectively, when H-3 was irradiated, indicating that H-3 and H-4 are in the *trans* disposition. The slow-moving spot was the 1,4-lactone **16**, obtained in 24% yield. NOE experiments were also used in assigning the product as the [3.3.0]bicyclic isomer **16** (Fig. 2). When H-6 was irradiated, NOE enhancement occurred at H-3 and H-4, indicating H-6 and H-3 to be on the same side of the ring. The lactone **16** showed a C=O stretching band at high frequency (1790 cm^{-1}) indicating a 1,4-lactone; the *C*-furanosyl derivative **17** shows its C=O stretching band at lower frequency (1740 cm^{-1}).

The stereoisomerically pure 4,5:6,7-diisopropylidenated (*E*)-unsaturated sugar **12** was obtained in moderate yield (20%) by direct reaction of D-arabinose with the ylide **5** and subsequent acetonation. Our previous work[7] has shown that the pure *trans* compound **12** is difficult to obtain from the reaction of 2,3:4,5-di-*O*-isopropylidene-*aldehydo*-D-arabinose with ylide **5**.

With D-*xylose* (**3**). The behavior of D-xylose, when treated with ylide **5**, followed by acetylation, was evidently quite similar to that of D-ribose. The desired unsaturated product **9** and a cyclized product **18**, which are analogues of **7** and **15**, were obtained in 43 and 32% yields, respectively, after the reaction sequence. Two products of low polarity, assigned as the acetonated analogues **13** (alkene, 18%) and **19** (lactone, 42%) were also obtained after protection by *O*-isopropylidenation. In the case of D-xylose, the *cis* relationship of the hydroxyl groups at C-5 and C-7 in the furanose ring of the cyclized product permitted *O*-isopropylidenation between the hydroxyl groups at C-5 and C-7.

With D-*lyxose* (**4**). Among the D-aldopentoses, D-lyxose gave the best yield of unsaturated sugar derivative under the same Wittig conditions. D-Lyxose underwent the Wittig reaction with **5** to give only one major product, the acetylated unsaturated sugar **10** (61%), or the diacetal **14** (34%), respectively, after protection by acetylation or isopropylidenation. Both **10** and **14** are *trans*-α,β-unsaturated esters. Neither cyclized products nor *cis* Wittig adducts were isolated from the reaction products.



27 **28** **29**

E/*Z* = 11:1, 73%

Scheme 2.

*With 2-deoxy-*D-erythro-*pentose* (**27**). Wittig alkenation of **27** with $Ph_3PCHCO_2CH_3$ (**5**) in boiling THF, followed by acetylation, gave a 73% yield of a separable mixture of the *trans*-α,β-unsaturated ester **28** ($J_{2,3}$ 15.7 Hz) and its (*Z*)-isomer **29** ($J_{2,3}$ 11.6 Hz) in 11 : 1 ratio.

Remarkably, no cyclized product was obtained from this reaction. This result may imply that the hydroxyl group at position 2 of the sugar plays an important role in the Michael addition to the Wittig adduct. Similar work by Rokach and co-workers[17] reported only the *trans* product being obtained in refluxing benzene with one equivalent of the ethoxy ylide (Ph_3PCHCO_2Et) and **27**. However when two equivalents of ylide were used, only a cyclized product, the *C*-glycofuranosyl derivative, was obtained.

General interpretations. The foregoing direct Wittig reactions of five aldopentoses (**I**) suggest that both *trans* (**IV**) and *cis* (**VI**) products are initially generated in the reaction with unprotected sugars, via the acyclic sugar (**II**) and four-membered cyclic intermediate (**III**), Fig. 3.

The *trans* isomers (**IV**) may undergo Michael addition, followed by ring closure (path a) to give cyclized products. Furthermore, the *cis* isomers (**VI**) may undergo either lactonization, followed by Michael addition (path c), or Michael addition followed by lactonization (path b), to afford the cyclized products. The most favored route to the cyclized products is indicated to be path c by the fact that no cyclized product was obtained with the 2-deoxy sugar **27**.

Wittig reaction of unprotected D-*aldopentoses in the presence of* $Cu(OAc)_2$.—In order to hinder the formation of cyclized products, it is desirable to protect the hydroxyl groups in the intermediates **IV** or **VI** (Fig. 3) as soon as they are formed. Attempts to diminish the extent of intramolecular cyclization were made by incorporating an equivalent amount of copper acetate in the reaction medium. Complex formation between metal ions and carbohydrates is a well known phenomena[18]. In a complicated reaction leading to an equilibrium mixture of products, metal ions may form complexes with not only the starting material (sugars) but also with reaction products (for example **IV** and **VI**), and may thus change the net outcome of the reaction. It was postulated that complex formation between a metal ion and the unsaturated sugar product might suppress intramolecular

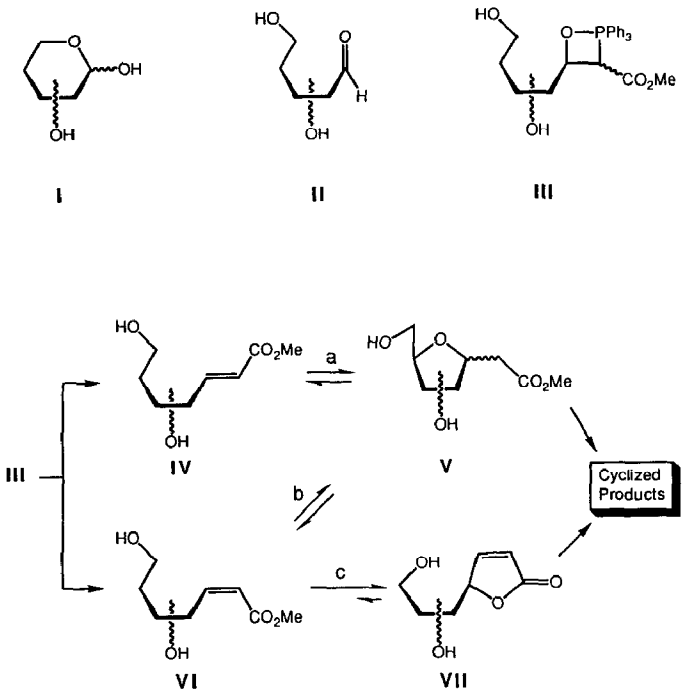
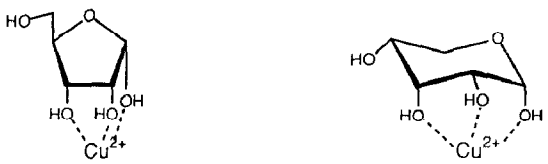


Fig. 3. Mechanistic pathways for the Wittig reaction of unprotected D-aldopentoses.

Michael addition. Consequently the Wittig reaction of unprotected sugars was repeated with incorporation of metal ions in the medium. Angyal[18] has pointed out the strong complexing ability of Cu^{2+} with sugars, and in consequence this cation was used.

When a suspension of D-ribose was treated with the ylide **5** in the presence of one equivalent of copper(II) acetate in boiling THF, no Wittig alkenation occurred and only peracetylated β-D-ribopyranose (**20**, 89%) was isolated after conventional acetylation (Scheme 1). When the same procedure was performed with *N,N*,-dimethylformamide as the solvent, the desired unsaturated sugar **7** was obtained but only in low yield (12%), and the peracetate **20** was again the major product (57%). No cyclized product **15** was found. The reason for this outcome may be readily rationalized by the fact that the anomeric hydroxyl group in D-ribose is able to form a complex with copper ions. Strong complexing occurs between this cation and sugars that have a contiguous *a,e,a* sequence of hydroxyl groups in the pyranose ring, or a *cis, cis*-1,2,3-triol grouping in a five-membered ring[18]. Among the aldopentoses in organic solvents, D-ribose is exceptional in containing a considerable proportion of the furanose structure[19]. Both the α-furanose and α-pyranose forms of D-ribose have a favorable arrangement of hydroxyl groups (including the anomeric hydroxyl group) for complex formation (**30, 31**). Such complexation with the anomeric hydroxyl group may be expected to hinder the Wittig reaction. (Fig. 4).

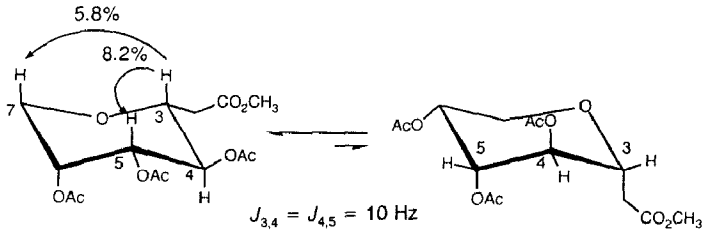


30 31

Fig. 4. Complex formation between D-ribose and copper(II) ion.

When the Wittig reaction was performed with D-arabinose in the presence of $Cu(OAc)_2$, the outcome was quite different from that observed in the absence of metal ion. The main product was the alkene **8**, obtained in high yield (50%) and almost double that obtained without $Cu(OAc)_2$. Accompanying the cyclized product was a Michael-addition product, a *C*-pyranosyl derivative (**21**), obtained in low yield (12%). No five-membered-ring cyclized product (**14** or **15**) was found. Noteworthy is the fact that the desired product, the unsaturated sugar **8**, was obtained in high yield as a result of depressing the internal Michael-addition reaction. The cyclized product was assigned as the α-*C*-glycopyranosyl derivative **21** by its ^{1}H NMR spectrum, which showed the H-3 proton as a doublet of doubled doublets at 3.85 ppm. By adopting the $^1C_4$ conformation as the preponderant conformer, the $J_{3,4}$ coupling constant was large (9.9 Hz). In addition, a large NOE increment at H-5 (8.2%) was observed when H-3 was irradiated, indicating that H-3 and H-5 are in the same plane (Fig. 5).

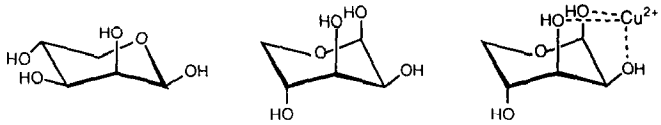
Because D-arabinose has no suitable arrangement of three hydroxyl groups to form a complex in the pyranose form, the starting material is not stabilized by complexation. However, such complexing with metal ions may be favored in the desired product, which has the *erythro–threo* configuration in the acyclic unsaturated sugar. Because the *erythro–threo* sequence of hydroxyl groups is more prone to complex formation than an *erythro* pair adjacent to a primary hydroxyl group sequence[20], the primary hydroxyl group may not be complexed in the acyclic Wittig adduct, and would thus be able to form the intramolecular Michael adduct **21** observed as a minor product.



$J_{3,4} = J_{4,5} = 10$ Hz

21

Fig. 5. NOE enhancement of compound **21**.



$^4C_1$ $^1C_4$ 32

Fig. 6. Complex formation pattern of D-lyxopyranose and copper(II) ion.

D-Xylose also showed an increased yield (49%) in the desired product **9** in the Wittig reaction when $Cu(OAc)_2$ was present. The cyclized product **23**, and unreacted peracetylated α- and β-D-xylopyranose **22**, which were difficult to separate, were also determined to be formed in 4.2 and 8.8% yields, respectively, by ^1H NMR spectroscopy. The adduct **23** was assigned as the β-*C*-glycopyranosyl derivative by ^1H NMR spectroscopy, which showed the H-3 proton as a doublet of triplets at 3.83 ppm with a large coupling constant ($J_{3,4}$ 9.9 Hz). The large value of $J_{3,4}$ indicated H-3 and H-4 to be in *trans*-diaxial disposition and provided convincing evidence that **23** was a β-*C*-glycosyl compound. It is not clear why some starting D-xylose remained unreacted, because it has no hydroxyl-group sequence favorable for formation of a complex that would involve the anomeric hydroxyl group in the pyranose form.

The metal-ion effect on the Wittig reaction with D-lyxose was similar to that with D-ribose. The main product was the desired unsaturated alkene **10**, formed in 40% yield. Peracetylated α- and β-D-lyxopyranose **24** was also obtained as a byproduct in 20% yield after acetylation. D-Lyxose has the *a,e,a* sequence of hydroxyl groups in the β-pyranose form **32**, including the anomeric hydroxyl group (see Fig. 6). However D-lyxose does not possess this advantageous complexing site in its most favorable conformation ($^4C_1$ of the β anomer) but only in a less favored one ($^1C_4$). Therefore D-lyxose might form a complex involving the anomeric position to a lesser extent than D-ribose, and consequently the proportion of unreacted starting material would be smaller than observed with D-ribose.

In conclusion, the Wittig reaction of unprotected aldopentoses has the merit of forming the *E*-alkene stereoselectively, as well as decreasing the number of preparative reaction steps. The formation of cyclized byproducts through internal Michael addition may be diminished by incorporating $Cu(OAc)_2$ in the reactions with D-arabinose and D-xylose, which are the most readily available D-aldopentoses. Optimal preparative yield of the *trans*-2,3-unsaturated tetraacetate products directly from the parent aldopentoses are thus 25% (**7**, *ribo*), 50% (**8**, *arabino*), 49% (**9**, *xylo*), and 61% (**10**, *lyxo*).

EXPERIMENTAL

General methods.—Melting points were determined using a Thomas–Hoover Unimelt apparatus and are uncorrected. Optical rotations were measured with a

TABLE I

^{1}H NMR spectral data for unsaturated Wittig products from D-aldopentoses

Compd	Chemical shift (δ) and coupling constants								
	H-2 $J_{2,3}$	H-3 $J_{2,4}$	H-4 $J_{3,4}$	H-5 $J_{4,5}$	H-6 $J_{5,6}$	H-7 $J_{6,7}$	H-7′ $J_{7,7'}$, $J_{6,7'}$	OCH_3	CH_3
7	5.89dd 15.7	6.78dd 1.7	5.59dd 5.4	5.22dd 3.6	5.13ddd 7.3	4.22dd 2.8	4.07dd 12.3, 5.1	3.65s	1.94–2.02 4s
8	5.94dd 15.8	6.76dd 1.8	5.68m 4.8	5.38dd 3.0	5.19ddd 8.6	4.24dd 2.7	4.13dd 12.5, 4.7	3.72s	2.04–2.12 4s
9	5.87dd 15.8	6.74dd 1.7	5.51ddd 5.2	←5.23–5.18m→ 5.2	 4.7	4.21dd 4.7	3.89dd 12.0, 5.8	3.65s	1.95–2.05 4s
10	5.91dd 15.7	6.75dd 1.4	5.49dd 6.3	5.31dd 6.9	5.37m 3.4	4.22dd 4.9	3.96dd 11.7, 6.5	3.73	2.03–2.08 4s
11	6.15dd 15.6	7.04dd 1.8	4.83ddd 4.5	4.14dd 6.8	←3.85–4.06m→ 6.5			3.74s	1.29–1.47 4s
12	6.13dd 15.7	6.97dd 1.7	4.49ddd 4.5	3.64t 7.7	3.90m 7.7	←4.02–4.11m→		3.70s	1.30–1.37 4s
13	6.14dd 15.6	6.88dd 1.4	4.49dd 5.7	3.83m 8.1	4.20dt	4.04dd 6.8	3.83m 8.3	3.75s	1.38–1.45 4s
14	6.09dd 15.6	6.80dd 1.3	4.69dt 6.8	4.23dd 6.7	4.06dd 7.6	3.98dd 6.5	3.59dd 8.0, 7.1	3.76s	1.35–1.57 4s
28	5.79dt 15.6	6.81dt 1.3	2.51m [a] 7.3	←5.08–5.21m→		4.26dd 3.2	4.12dd 12.3, 5.8	3.70s	2.02–2.06 3s
29	5.88dt 11.5	6.18dt 1.7	3.03m [a] 7.3	←5.11–5.23m→		4.30dd 3.3	4.17dd 12.2, 6.2	3.69s	2.03–2.06 3s

[a] 2 H for H-4 and H-4′.

Perkin–Elmer model 141 polarimeter at 25°C unless otherwise noted. Reaction solvents were purified and dried by distillation as recommended[21]. TLC was performed on precoated glass plates of Silica Gel 60F-254 (E. Merck), and compounds on the plate were detected by spraying with 10% aq H_2SO_4 solution with subsequent heating. Flash-column chromatography was performed on 230–400 mesh silica gel (E. Merck) as described in the literature[22]. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker AM 250 (250 MHz ^{1}H, 62.5 MHz ^{13}C), WM 300 (300 MHz ^{1}H, 75 MHz ^{13}C), and AM 500 (500 MHz ^{1}H, 125 MHz ^{13}C) spectrometers for solutions in $CDCl_3$, unless otherwise specified. Chemical shifts (ppm) are relative to Me_4Si as the internal standard. Splitting patterns are designated: s, singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet. Mass spectra were obtained at The Ohio State University Chemical Instrument Center by use of a VG 70-250S mass spectrometer with FAB ionization. Infrared spectra were obtained with a Mattson Polaris FT-IR instrument. Microanalyses were performed by Atlantic Microlab, Inc.

Typical procedure for the Wittig reaction of unprotected D-*aldopentoses.*

*Methyl (*E*)-4,5,6,7-tetra-*O*-acetyl-2,3-dideoxy-*D*-ribo-hept-2-enonate* (**7**) *and 5,7-di-*O*-acetyl-3,6-anhydro-2-deoxy-*D*-altro-heptonic acid 1,4-lactone* (**15**).—To a suspension of D-ribose (1.5 g, 10 mmol) in 60 mL of THF was added methyl (triphenylphosphoranylidene)acetate (**5**, 3.8 g, 11 mmol), and the mixture was boiled under reflux for 2 h at 85°C. The mixture turned clear (~ 4 h later), and the refluxing was continued overnight (17 h). TLC (3:1 $CHCl_3$–MeOH) showed two product spots (R_f 0.63 and 0.52) and no starting material (R_f 0.1). The solvent was evaporated to give a syrup. Water (50 mL) was added to the syrup to give a precipitate. The precipitate (byproduct Ph_3PO) was filtered and the filtrate was washed with $CHCl_3$ (2 × 15 mL). The aqueous layer was evaporated to give a syrup. The syrup was dissolved in pyridine (3 mL) and was treated with Ac_2O (3 mL) at 0°C. After stirring for 3 h at room temperature, the mixture was quenched with ice–water (40 mL) and was extracted with $CHCl_3$ (3 × 30 mL). The combined organic layer was washed successively with 5% HCl, satd aq $NaHCO_3$, water, and dried (Na_2SO_4). Filtration and evaporation gave a syrup (2.45 g) that showed four product spots in TLC. Two major spots (R_f 0.55 and 0.31, 1:1 EtOAc–hexanes) were separated by flash chromatography (1:2 EtOAc–hexanes, column size 25 mm × 70 cm). The fast-moving spot gave the unsaturated ester **7** (750 mg, 20%), and the other major spot gave the lactone **15** (1.28 g, 56.6%).

Compound **7** was a syrup; $[\alpha]_D$ + 18° (*c* 0.5, CH_2Cl_2); for ^1H NMR and ^{13}C NMR data, see Tables I and III; MS: *m/z* (rel. intensity): 375 (7.7, M + 1), 315 (100, 375 – AcOH), 273 (19.5, 315 – CH_2CO), 241 (21.3, 273 – MeOH), 213 (22.2, 273 – AcOH), 171 (21.2, 213 – CH_2CO), and 153 (56.8, 213 – AcOH); IR (neat) 2950, 1760, 1660, 1440, 1375, 1055, 985 cm^{-1}. Anal. Calcd for $C_{16}H_{22}O_{10}$ (374.36): C, 51.34; H, 5.92. Found: C, 51.36; H, 5.94.

Compound **15** was a syrup; $[\alpha]_D$ + 185° (*c* 0.94, CH_2Cl_2); for ^1H NMR and ^{13}C NMR data, see Tables II and IV; MS: *m/z* (rel. intensity): 259 (100, M + 1), 217 (44.7, 259 – CH_2CO), 199 (74.1, 259 – AcOH), 139 (48.2, 199 – AcOH), and 85 (41.2).; IR (neat) 2950, 1780 (lactone C=O), 1740, 1365, 1230, 1100, 1040 cm^{-1}. Anal. Calcd for $C_{11}H_{14}O_7$ (258.23): C, 51.16; H, 5.46. Found: C, 51.36; H, 5.45.

*Methyl (*E*)-4,5,6,7-tetra-*O*-acetyl-2,3-dideoxy-*D*-arabino-hept-2-enonate* (**8**) *and 5,7-di-*O*-acetyl-3,6-anhydro-2-deoxy-*D*-gluco-heptonic acid 1,4-lactone* (**16**) *and methyl 4,5,7-tri-*O*-acetyl-3,6-anhydro-2-deoxy-*D*-manno-heptonate* (**17**).—The same procedures were used just as described, starting from D-arabinose. The enonate **8** (obtained in 26% yield) had mp 116°C (Pr^iOH); $[\alpha]_D$ + 37.6° (*c* 1.0, $CHCl_3$); lit.[7] mp 116–117°C, $[\alpha]_D$ + 35° ($CHCl_3$); all other spectral data were the same as already described[7] for **8**.

Lactone **16** was a syrup; yield 24%; $[\alpha]_D$ −53.6° (*c* 0.9, CH_2Cl_2); for ^1H NMR and ^{13}C NMR data, see Tables II and IV; MS: *m/z* (rel. intensity): 259 (100, M + 1), 217 (32.9, 259 – CH_2CO), 199 (15.3, 259 – AcOH), 157 (11.2, 217 – AcOH), and 139 (23.0, 199 – AcOH); IR (neat), 2960, 1790, 1750, 1740, 1370, 1240,

1040 cm^{-1}. Anal. Calcd for $C_{11}H_{14}O_7$ (258.23): C, 51.16; H, 5.46. Found: C, 51.12; H. 5.50.

The anhydro ester **17** was a syrup; yield 25%; $[\alpha]_D$ + 15.7° (*c* 0.75, CH_2Cl_2); for ^1H NMR and ^{13}C NMR data, see Tables II and IV; MS: *m/z* (rel. intensity): 333 (84.1, M + 1), 291 (15.3, 333 – CH_2CO), 273 (79.1, 333 – AcOH), 259 (62.7, 291 – MeOH), 199 (23.5, 259 – AcOH), 213 (9.41, 273 – AcOH), 153 (100, 213 – AcOH), and 139 (63.4, 199 – AcOH).; IR (neat), 2970, 1740, 1440, 1370, 1230, 1040 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_9$ (332.31): C, 50.60; H, 6.07. Found: C, 50.68; H, 6.10.

*Methyl (*E*)-4,5,6,7-tetra-*O*-acetyl-2,3-dideoxy-*D*-xylo-hept-2-enonate* (**9**) *and 5,7-di-*O*-acetyl-3,6-anhydro-2-deoxy-*D*-ido-heptonic acid 1,4-lactone* (**18**).—The same procedures were used as described, starting from D-xylose. The enonate **9** (obtained in 43% yield) had mp 75–76°C (EtOH); $[\alpha]_D$ + 13.6° (*c* 0.7, CH_2Cl_2); for ^1H NMR and ^{13}C NMR data, see Tables I and III; IR (KBr pellet) 1740, 1720, 1435, 1370, 1235 cm^{-1}; MS: *m/z* (rel. intensity): 375 (12.2, M + 1), 315 (100, 375 – AcOH), 273 (12.2, 315 – CH_2CO), 241 (16.0, 273 – MeOH), 213 (17.8, 273 – AcOH), 171 (13.7, 213 – CH_2CO), 153 (56.8, 213 – AcOH), and 103 (18.01). Anal. Calcd for $C_{16}H_{22}O_{10}$ (374.36): C, 51.34; H, 5.92. Found: C, 51.45; H, 5.96.

Compound **18** (yield 32%) had mp 59.5–60.5°C; $[\alpha]_D$ + 55° (*c* 0.82, CH_2Cl_2); for ^{1} H NMR and ^{13}C NMR data, see Tables II and IV; MS: *m/z* (rel. intensity): 259 (55.02, M + 1), 217 (10.6, 259 – CH_2CO), 199 (100, 259 – AcOH), 139 (68.2, 199 – AcOH), and 81 (23.2, 139 – Me_2CO). Anal. Calcd for $C_{11}H_{14}O_7$ (258.23): C, 51.16; H, 5.46. Found: C, 51.33; H, 5.48.

*Methyl (*E*)-4,5,6,7-tetra-*O*-acetyl-2,3-dideoxy-*D*-lyxo-hept-2-enonate* (**10**).—The same procedures were used just as described in synthesis of **7** and **15**, but starting from D-lyxose. The enonate **10** obtained in 61% yield was a syrup; $[\alpha]_D$ + 18.0° (*c* 1.1, $CHCl_3$); for ^1H NMR and ^{13}C NMR data, see Tables I and III; IR (neat) 2960, 1750, 1730, 1660, 1440, 1375, 1220, and 1050 cm^{-1}; MS: *m/z* (rel. intensity): 375 (3.22, M + 1), 315 (100, 375 – AcOH), 273 (14.0, 315 – CH_2CO), 241 (19.8, 273 – MeOH), 213 (22.6, 273 – AcOH), 171 (17.9, 213 – CH_2CO), 153 (48.9, 213 – AcOH), 139 (26.8), and 103 (20.3). Anal. Calcd for $C_{16}H_{22}O_{10}$ (374.36): C, 51.34; H, 5.92. Found: C, 51.27; H, 5.94.

*Methyl (*Z*)-5,6,7-tetra-*O*-acetyl-2,3,4-trideoxy-*D*-erythro-hept-2-enonate* (**29**), *and methyl (*E*)-5,6,7-tetra-*O*-acetyl-2,3,4-trideoxy-*D*-erythro-hept-2-enonate* (**28**).—The same procedures were used just as described in synthesis of **7** and **15**, but starting from 2-deoxy-D-*erythro*-pentose (**27**). Flash chromatography (eluent, 1:2 EtOAc–hexanes) gave the *cis* product **29** (R_f 0.55, 1:1 EtOAc–hexanes, 6.1%), and *trans* product **28** (R_f 0.46, 1:1 EtOAC–hexanes, 66.5%); total yield, 72.6%.

Compound **29** had $[\alpha]_D$ + 13.2° (*c* 2, CH_2Cl_2); for ^1H NMR and ^{13} C NMR data, see Tables I and III; MS: *m/z* 317 (14.7, M + 1), 257 (100, M + 1 – AcOH), 243 (23.5), 197 (8.0, 257 – AcOH), 183 (12.3), 155 (33.1), 137 (97.2, 197 – AcOH), 123 (44.7). Anal. Calcd for $C_{14}H_{20}O_8$ (316.31): C, 53.16; H, 6.37. Found: C, 53.06; H, 6.39.

TABLE II

^{1}H NMR spectral data for the cyclized products from D-aldopentoses

Compd	Chemical shift (δ) and coupling constants										
	H-2 $J_{2,3}$	*H-2'* $J_{2',2}$	*H-3* $J_{2,3}$	*H-4* $J_{3,4}$	H-5 $J_{4,5}$	H-6 $J_{5,6}$	H-7 $J_{6,7}$	H-7' $J_{7,7'}$, $J_{6,7'}$	OCH_3	$COCH_3$	CMe_2
15	2.69dd 1.2	2.80dd 18.8	4.90ddd 6.4	5.18dd 4.7	4.94dd 4.8	4.19ddd 8.3	4.34dd 4.9	4.10dd 12.2, 2.8		2.03, 2.08	
16	2.67dd 2.1	2.73dd 16.2	4.82m 3.4	4.86d 4.2	5.16d 0	4.12m 4.0	4.31dd 3.0	4.16dd 11.2, 5.0		2.04, 2.08	
17	⟵ 2.68d ⟶ 3.5		4.43dt 6.8	⟵ 5.06–5.10m ⟶ 3.5		⟵ 4.16–432m ⟶			3.66	2.05, 2.06 [a]	
18	2.68dd 2.2	2.76dd 18.8	4.96ddd 4.7	4.87d 4.5	5.46d 0	4.37m 3.6	4.21dd 4.8	4.14dd 11.6, 6.9		2.07, 2.12	
19	2.67dd 1.6	2.74dd 18.7	5.03m 5.1	4.85d 4.2	4.52d 0	3.91dd 2.3	3.98dd 0	4.07dd 13.5, 2.5			1.39, 1.46
21	2.50dd 4.1	2.60dd 15.7	3.85ddd 8.3	5.15t 9.9	5.04dd 10.0	5.30m 3.5	3.66dd 2.0	3.98dd 13.3, 1.1	3.70	2.13, 2.04 1.99	
23	⟵ 2.47d ⟶ 6.1		3.83dt 6.1	4.85t 9.9	5.15dd 9.5	4.94m 9.4	4.13dd 8.4	3.59dd 12.0, 5.0	3.68	2.01–2.03	

[a] Integrates for 6 H.

TABLE III

^{13}C NMR spectral data for unsaturated Wittig products from D-aldopentoses

Compd	Chemical shifts (δ)											
	C-1	C-2	C-3	C-4 [a]	C-5 [a]	C-6 [a]	C-7	OMe	$COCH_3$	$COCH_3$	CMe_2	CMe_2
7	165.5	122.9	140.1	70.4	70.3	68.5	61.4	51.5	169.1, 169.3 169.5, 170.1	20.3 [b] 20.4, 20.5		
8	165.6	123.2	140.9	69.7	69.5	68.2	61.7	51.8	170.5, 169.7 169.5, 169.4	20.5 [b] 20.6, 20,7		
9	165.5	123.3	140.3	70.2	70.1	68.5	61.6	51.7	169.1, 169.4 169.5, 170.1	20.3, 20.4 20.5 [b]		
10	165.6	124.5	140.4	70.5	68.1	69.5	61.7	51.8	169.1, 169.6 169.8, 170.3	20.6 [b] 20.7 [b]		
11	166.4	128.1	143.7	78.8	76.5	73.8	67.4	51.5			109.6 [b]	27.4, 26.7 25.2, 25.1
12	166.5	120.9	145.3	81.8	76.9	78.9	67.4	51.5			110.2 109.8	26.9, 26.7 26.6, 25.1
13	166.1	122.5	144.1	80.3	74.3	76.3	65.4	51.6			110.3 109.8	26.7, 26.6 26.0, 25.3
14	165.9	123.6	142.4	79.9	75.8	74.9	65.7	51.7			110.3 109.8	27.5, 26.5 25.1 [b]
28	166.2	124.2	142.5	33.1	71.2	69.8	61.7	51.6	170.5, 169.9 169.8	20.8 [b] 20.7		
29	165.2	122.1	143.3	29.6	71.3	70.8	61.8	51.1	169.9 170.5 [b]	20.6 20.8 [b]		

[a] These resonances may be interchanged for **7**–**14**. [b] Resonances from two ^{13}C-atoms are indicated.

TABLE IV

^{13}C NMR spectral data for the cyclized products from D-aldopentoses

Compd	Chemical shifts (δ)											
	C-1	C-2	C-3 [a]	C-4 [a]	C-5 [a]	C-6 [a]	C-7	OMe	$COCH_3$	$COCH_3$	CMe_2	CMe_2
15	174.6	36.2	76.7	80.2	76.7	72.9	62.7		170.0, 170.3	20.4, 20.6		
16	174.0	35.9	78.2	83.3	86.9	77.6	63.1		170.5, 169.5	20.4, 20.5		
17	169.9	37.6	80.8	80.2	79.6	78.4	63.1	51.8	169.8, 170.4 170.6	20.6 [b]		
18	174.3	35.6	85.3	77.0	77.0	75.1	61.4		169.2, 170.3	20.4, 20.6		
19	175.1	35.9	87.0	77.2	72.5	72.2	60.2				97.7	28.6, 28.9
21	170.8	37.3	75.4	71.6	69.2	68.8	68.0	51.9	170.3, 170.1 169.8	20.9, 20.7 20.6		

[a] These resonances may be interchanged. [b] Resonances of three ^{13}C atoms indicated.

TABLE V

Wittig reaction of unprotected D-aldopentoses [a]

D-Pentose	Yields (%)			
	Without $Cu(OAc)_2$		With $Cu(OAc)_2$	
	Unsaturated products	Cyclized products	Unsaturated products	Cyclized products
Ribose	25	57	12	[b]
Arabinose	26	49	50	12
Xylose	43	32	49	4
Lyxose	61	–	40	[b]

[a] Isolated yields of peracetylated products. [b] Tetraacetates of D-aldopentoses were found.

Compound **28** had $[\alpha]_D$ + 17.2° (*c* 2, CH_2Cl_2); for ^1H NMR and ^{13}C NMR data, see Tables I and III; MS: *m/z* 317 (26.6, M + 1), 257 (100, M + 1 – AcOH), 243 (43.9), 201 (12.0), 183 (13.4), 155 (19.1), 123 (26.8), 95 (13.9). Anal. Calcd for $C_{14}H_{20}O_8$ (316.31): C, 53.16; H, 6.37. Found: C, 53.26; H. 6.34.

General procedure for the preparation of di-O-isopropylidenated unsaturated sugars (**11–14**).—To a suspension of the D-aldopentose (3.0 g, 20 mmol) in 80 mL of THF, methyl (triphenylphosphoranylidene)acetate (**5**, 7.35 g, 22.5 mmol) was added, and the mixture was boiled under reflux overnight. The solvent was evaporated to give a syrup that was treated with 100 mL of water. The resulting precipitate Ph_3PO was filtered off, and the filtrate was washed with $CHCl_3$ (30 mL). The aqueous layer was evaporated to give a syrup that was dissolved into DMF (30 mL). To the mixture was added 2,2-dimethoxypropane (**6**, 4.7 g, 45 mmol) and TsOH (100 mg, monohydrate), and stirring was continued at 90° overnight. The mixture was made neutral with Amberlite IRA-400 (OH^-) resin. Filtration and evaporation of the solvent gave a syrup. Flash chromatography of the syrup (1:4 EtOAc–hexanes) afforded the respective products.

Methyl (E)-2,3-dideoxy-4,5:6,7-di-O-isopropylidene-D-ribo-hept-2-enonate (**11**).—Compound **11** was a liquid; yield 29%; $[\alpha]_D$-35.2° (*c* 1.5, CH_2Cl_2); for ^1H NMR and ^{13}C NMR data, see Tables I and III; MS: *m/z* (rel. intensity): 287 (7.3, M + 1), 271 (37.4, M – CH_3), 229 (13.9, 287 – Me_2CO), 227 (18.8, 271 – CO_2), 171 (19.2, 229 – Me_2CO), 139 (22.1), and 101 (100, $C_5H_9O_2$). Anal. Calcd for $C_{14}H_{22}O_6$ (286.16): C, 58.73; H, 7.75. Found: C, 58.81; H, 7.76.

Methyl (E)-2,3-dideoxy-4,5:6,7-di-O-isopropylidene-D-arabino-hept-2-enonate (**12**).—Compound **12** was a liquid; yield 20%; $[\alpha]_D$ – 1.6° (*c* 1.0, $CHCl_3$); lit.[7] $[\alpha]_D$ – 1.5 (*c* 0.6, $CHCl_3$); for ^1H NMR and ^{13} C NMR data, see Tables I and III; IR (neat) 2990, 1730, 1660, 1370, 1060 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_6$ (286.16): C, 58.73; H, 7.75. Found: C, 58.66; H, 7.77.

Methyl (E)-2,3-dideoxy-4,5:6,7-di-O-isopropylidene-D-xylo-hept-2-enonate (**13**) *and 5,7-O-isopropylidene-3,6-anhydro-2-deoxy-D-ido-heptonic acid 1,4-lactone* (**19**). —Alkene **13** was a liquid; yield 18%; $[\alpha]_D$ – 16.8° (*c* 1, $CHCl_3$); for ^1H NMR and ^{13}C NMR data, see Tables I and III; MS: *m/z* (rel. intensity): 287 (13.7, M + 1),

271 (41.4, M − CH_3), 229 (36.3, 287 − Me_2CO), 171 (21.2, 229 − Me_2CO), 153 (20.3, 171 − H_2O), and 101 (100, $C_5H_9O_2$); IR (neat) 2995, 1730, 1660, 1440, 1370 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_6$ (286.16): C, 58.73; H, 7.75. Found: C, 58.80; H, 7.79.

Lactone **19** had mp 105.5–106°C (EtOH); yield 42%; $[\alpha]_D$ + 50.8° (*c* 1.2, CH_2Cl_2); for ^1H NMR and ^{13}C NMR data see Tables II and IV; IR (KBr pallet), 2980, 2920, 2880, 1770 (C=O, lactone), 1370 cm^{-1}; MS: *m/z* (rel. intensity): 215 (100, M + 1), 157 (22.5, 215 − Me_2CO), 135 (24.8), 119 (23.7), and 85 (33.1). Anal. Calcd for $C_{10}H_{14}O_5$(214.22): C, 56.07; H, 6.59. Found: C, 56.11; H, 6.60.

*Methyl (*E*)-2,3-dideoxy-4,5:6,7-di-*O*-isopropylidene-*D*-lyxo-hept-2-enonate* (**14**).—Compound **14** had mp 86°C (MeOH); yield 34%; $[\alpha]_D$ − 1.5° (*c* 1.7, CH_2Cl_2); for ^1H NMR and ^{13}C NMR data, see Tables I and III; MS *m/z* (rel. intensity): 287 (50.9, M + 1), 271 (39.7, M − CH_3), 229 (98.5, 287 − Me_2CO), 171 (35.2, 229 − Me_2CO), 129 (36.4, 171 − CH_2CO), and 101 (100, $C_5H_9O_2$). Anal. Calcd for $C_{14}H_{22}O_6$(286.16): C, 58.73; H, 7.75. Found: C, 58.64; H. 7.74.

Typical procedure for the Wittig reaction in the presence of $Cu(OAc)_2 \cdot H_2O$.

Enonate **8** *and methyl 4,5,6-tri-*O*-acetyl-3,7-anhydro-2-deoxy-*D*-manno-heptonate* (**21**).—To a stirred solution of D-arabinose (750 mg, 5 mmol) in 30 mL of DMF were added methyl (triphenylphosphoranylidene)acetate (**5**, 2 g, 6 mmol) and $Cu(OAc)_2 \cdot H_2O$ (1 g, 5 mmol), and stirring was continued for 5 h at 90°C. TLC showed two product spots at R_f 0.6 and 0.52 (1:5 MeOH–$CHCl_3$). The solvent was evaporated to give a syrup. To the syrup was added water (40 mL), and the resulting precipitate (Ph_3PO) was filtered off. The filtrate was washed with $CHCl_3$ (30 mL), and the aqueous layer was evaporated to give another syrup, which was dissolved in 4 mL of pyridine and treated with 4 mL of Ac_2O at 0°C, and stirred at room temperature for 2 h. The mixture was quenched with 50 mL of ice–water and extracted with $CHCl_3$ (3 × 30 mL). The combined extracts were washed successively with 5% HCl, satd $NaHCO_3$, brine, water, and then dried (Na_2SO_4). Filtration and evaporation gave a solid (1.47 g), which showed two major spots on TLC (R_f 0.56, 0.47; 1:1 EtOAc–hexanes). Flash chromatography of this mixture led to compound **8** (940 mg, 50.3%) and **21** (210 mg, 12.6%).

Compound **21** was a syrup; $[\alpha]_D$ − 22.4° (*c* 1.2, $CHCl_3$); for ^1H NMR and ^{13}C NMR data, see Tables II and IV; IR (neat), 2980, 1745, 1440, 1360, 1220, 1040 cm^{-1}; MS *m/z* (rel. intensity): 333 (44, M + 1), 301 (8.1, 333 − CH_3OH), 273 (100, 333 − AcOH), 259 (19.5, 301 − CH_2CO), 231 (16.2, 273 − CH_2CO), 213 (10.8, 273 − AcOH), 199 (14.3, 259 − AcOH), 153 (98.2, 213 − AcOH), and 139 (43.8, 199 − AcOH).

Enonate **7** *and 1,2,3,4-tetra-*O*-acetyl-β-*D*-ribopyranose* (**20**).—The same reaction as above was performed but with D-ribose to give enonate **7** (R_f 0.55, 1:1 EtOAc–hexanes, 12%) and **20** (R_f 0.46; 1:1 EtOAc–hexanes, 57%). Compound **20** had mp 111–112°C; lit.[23] mp 112–113°C

Enonate **9** *and methyl 4,5,6-tri-*O*-acetyl-3,7-anhydro-2-deoxy-*D*-gulo-heptonate* (**23**) *and 1,2,3,4-tetra-*O*-acetyl-α- and β-*D*-xylopyranose* (**22**).—The same reaction

as above was performed but with D-xylose to give enonate **9** (R_f 0.52, 1:1 EtOAc–hexanes, 49%) and a mixture of **20** and tetraacetate **22** (R_f 0.63; 1:1 EtOAc–hexanes, 5.2 and 8.8%, respectively, by ^{1}H NMR spectroscopy).

Enonate **10** *and 1,2,3,4-tetra-*O*-acetyl-α- and β-*D*-lyxopyranose* (**24**).—The same reaction as above was performed but with D-lyxose to give a mixture of enonate **10** and tetraacetate **24** (R_f 0.52, 1:1 EtOAc–hexanes). The ^{1}H NMR spectrum of the unseparable mixture showed that the major product **10** (40%) was contaminated by tetraacetate **24** (11%).

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