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Note

Synthesis of feruloylated and *p*-coumaroylated methyl glycosides

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There has been an expansion of the research effort directed at discerning the role of hydroxycinnamic acids in plant cell-wall development and degradation [1–5]. It is well documented that ferulic acid (4-hydroxy-3-methoxy-*trans*-cinnamic acid) and *p*-coumaric acid (4-hydroxy-*trans*-cinnamic acid) are esterified to the primary position of α-L-arabinofuranosyl units of arabinoxylans in plants of the Gramineae[6–9]. Ferulic acid has also been reported to be esterified to D-galactosyl units of spinach pectin[10] and to the C-4 position of D-xylopyranosyl units of bamboo xyloglucans[11]. Studies with grasses have shown that rumen microflora release free hydroxycinnamic acids from cell walls[12], while other investigations have indicated that free and combined acids can reduce the digestibility of forage cell-wall components[13,14]. As hydroxycinnamic acids can also be covalently attached to lignin either through ester or ether linkages[15–17], these difunctional molecules may provide a cross-link between lignin and polysaccharides which would ultimately influence both cell-wall development and degradation. Clearly, hydroxycinnamic acids contribute extensively to the chemical aspects of the plant cell wall.

We have recently turned our attention to determining the exact nature of the phenolic acid covalent interaction with lignin and polysaccharides and the influence of this interaction on plant cell-wall development and degradation. Our approach, which utilizes NMR spectroscopy, requires the synthesis and characterization of suitable model compounds and their use as substrates for isolated enzymes and rumen microbes. We desired a facile route to methyl glycosides with hydroxycinnamic acids esterified to the primary position. This note describes two

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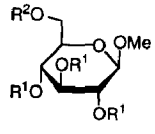
simple, high-yielding routes to several appropriately substituted glycosides. The methods are quite amenable to the synthesis of ^{13}C-labeled feruloylated and *p*-coumaroylated pyranosides and furanosides.

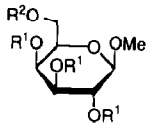
RESULTS AND DISCUSSION

The primary positions of methyl β-D-glucopyranoside (**1a**) and methyl β-D-galactopyranoside (**2a**) were readily available for acylation by the selective *O*-desilylation of **1b** and **2b** with methanolic potassium carbonate[18] as has been described[19,20]. Although the persilylated ethers were susceptible to degradation, **1c** and **2c** were quite stable (unless kept in solution for extended periods without adequate protection from moisture). The subsequent reaction of **1c** and **2c** with the 4-acetates of *p*-coumaroyl and feruloyl chlorides in pyridine afforded the crude silylated hydroxycinnamoyl carbohydrate esters (**1d** and **e**, and **2d** and **e**, respectively) which were *O*-desilylated by exposure to aqueous ethanol. This route provided the crystalline 4′-acetoxycinnamoyl pyranosides in good yields. The D-galactopyranosides **2f** and **2g** were prepared in greater than 80% overall yield based on **2a**. The overall yields of the D-glucopyranosides **1f** and **1g** were 45–50%, which was due to the susceptibility of **1b** to nonselective *O*-desilylation. Removal of the 4′-acetate to provide model compounds **1h** and **i**, and **2h** and **i** was achieved by treatment with 0.5 M piperidine or pyrrolidine in 95% ethanol.

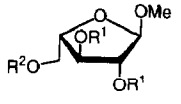
Removal of the trimethylsilyl group attached to the C-5 position of methyl 2,3,5-tri-*O*-trimethylsilyl-α-L-arabinofuranoside with K_2CO_3–methanol did not occur with any selectivity. Thus a different reaction scheme was developed to provide the hydroxycinnamic acid esters of **3a**. We have previously described an extremely simple synthesis of **3h** by taking advantage of the higher selectivity of the primary hydroxy group towards acylation[21]. However, the low yields (56%) were not suitable when ^{13}C-labeled hydroxycinnamoyl chlorides were used in the coupling step.



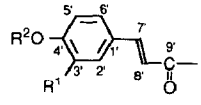
	R¹	R²
1a	H	H
1b	Me_3Si	Me_3Si
1c	Me_3Si	H
1d	Me_3Si	A
1e	Me_3Si	B
1f	H	A
1g	H	B
1h	H	C
1i	H	D
1j	Ac	A
1k	Ac	B



	R¹	R²
2a	H	H
2b	Me_3Si	Me_3Si
2c	Me_3Si	H
2d	Me_3Si	A
2e	Me_3Si	B
2f	H	A
2g	H	B
2h	H	C
2i	H	D
2j	Ac	A
2k	Ac	B



	R¹	R²
3a	H	H
3b	H	$^tBuMe_2Si$
3c	Ac	$^tBuMe_2Si$
3d	Ac	H
3e	Ac	A
3f	Ac	B
3g	H	C
3h	H	D



	R¹	R²
A	H	Ac
B	OMe	Ac
C	H	H
D	OMe	H

The strategy employed utilizes the synthesis of **3b**, the *O*-(*tert*-butyldimethylsilyl) derivative (TBDMS), which was available in 89% yield from **3a** with *tert*-butyldimethylsilyl chloride–pyridine. Protection of the remaining hydroxyl groups could be accomplished in the same reaction flask by the subsequent addition of acetic anhydride. Purification by silica gel chromatography gave **3c** in 84% yield from **3a**. Acetylation was the protection method of choice due to the simplicity of the one-pot silylation–acetylation sequence and the need for peracetylated materials for comparison with acetylated native cell-wall tissue isolates. Acetylation of isolated cell-wall fractions is a standard approach to improve native material solubility, which permits the solution NMR analysis of more concentrated samples.

Cleavage of the *tert*-butyldimethylsilyl group to expose the 5-hydroxyl group was accomplished in 83% yield by treatment with 80% acetic acid for 24 h. The crude product obtained from the one-pot silylation–acetylation sequence can also be submitted to the *O*-desilylation step, thus avoiding an intermediate chromatographic purification. Subsequent silica gel chromatography affords **3d** in greater than 70% overall yield from **3a**. This procedure is an improvement over previous preparations of methyl 2,3-di-*O*-acetyl-L- and D-arabinofuranosides[22,23], which relied upon formation of the 5-*O*-trityl derivative. Coupling of **3d** with the protected hydroxycinnamoyl chlorides in pyridine resulted in the formation of the peracetylated esters **3e** and **3f** in yields of up to 97%. Deacetylation of the fully protected L-arabinofuranoside esters was attempted with NaOMe–methanol (Zemplén method), piperidine–95% ethanol (50°), and pyrrolidine–95% ethanol (room temperature). The Zemplén deacetylation procedure resulted in 55–65% yield of the esters with the major byproducts being **1a** and the methyl hydroxycinnamate. The piperidine treatment resulted in about the same overall yield (60–65%), whereas the pyrrolidine treatment (0.5 M, 24 h) provided the deprotected models **3g** and **3h** in 73–83% yields. The ability to remove acetate protecting groups with piperidine or pyrrolidine in 95% ethanol without affecting the hydroxycinnamate bond is quite convenient. A cinnamic acid ester provides a relatively strong bond compared to that of an acetate[24], thus allowing differentiation of the two acyl groups. The use of cinnamoyl chloride in carbohydrate synthetic schemes warrants further study, especially in conjunction with standard acetate protection strategies.

The unambiguously assigned ^{13}C chemical shifts for several compounds are presented in Table I and are based on heteronuclear shift-correlated (HETCOR) spectroscopic experiments, with long-range ^{13}C-^{1}H correlation experiments used to assign the feruloyl-containing compounds. It is apparent that the aromatic sidechain carbons (C-7′, 8′, and 9′) are relatively insensitive to the carbohydrate and aryl moieties, as well as to acetylation. The C-7′ carbon resonances range from 144.8 to 146.1 ppm for samples in acetone-d_6. The C-8′ carbon resonances behave in a similar fashion, although there is a significant difference in the frequencies of the acetylated vs. free compounds (118.9–118.2 vs. 115.5–115.2 ppm, respectively). The unprotected feruloylated glycosides **1i**, **2i**, and **3h** exhibited C-8′ resonances upfield of C-5′ (115.5 vs. 116.0 ppm in acetone-d_6; 114.9 vs 115.9 ppm in 9:1

TABLE I

^{13}C-NMR chemical shifts for selected compounds [a,b]

Carbon [c]	Chemical shifts (ppm)															
	D-Glucopyranosyl						D-Galactopyranosyl						L-Arabinofuranosyl			
	Coumaroyl			Feruloyl			Coumaroyl			Feruloyl			Coumaroyl		Feruloyl	
	1f*	**1h**	**1j**	**1g***	**1i**	**1k**	**2f***	**2h**	**2j**	**2g***	**2i**	**2k**	**3e**	**3g**	**3f**	**3h**
1	103.9	104.8	102.0	103.9	104.8	102.0	104.4	105.2	102.5	104.4	105.3	102.4	107.5	110.2	107.5	110.3
2	73.6	74.5	72.0	73.6	74.6	72.0	73.3	72.0	69.6	73.3	72.0	69.5	82.0	83.1	82.0	83.2
3	76.4	77.6	73.5	76.4	77.7	73.6	70.9	74.4	71.7	71.0	74.4	71.7	78.0	79.2	78.1	79.3
4	70.4	71.2	69.6	70.3	71.2	69.5	69.1	69.7	68.4	69.1	69.6	68.3	81.2	82.3	81.3	82.4
5	73.9	74.7	72.3	73.9	74.8	72.3	72.9	73.3	71.4	72.9	73.3	71.4	64.0	64.7	63.9	64.8
6	64.1	64.2	63.0	64.0	64.2	62.9	64.3	64.0	62.3	64.3	64.0	62.3	–	–	–	–
1′	132.3	126.7	132.8	133.7	127.3	134.1	132.2	126.6	132.7	133.7	127.3	133.9	132.7	126.8	134.0	127.4
2′	130.0	130.9	130.2	112.2	111.2	112.3	130.0	130.9	130.2	112.2	111.3	112.2	130.1	130.9	112.3	111.2
3′	122.8	116.6	123.2	151.6	148.7	152.7	122.8	116.7	123.2	151.7	148.7	152.5	123.2	116.6	152.5	148.7
4′	152.7	160.6	153.5	141.7	150.0	142.7	152.6	160.5	153.5	141.7	150.1	142.6	153.4	160.5	142.6	150.1
5′	122.8	116.6	123.2	123.7	116.0	124.1	122.8	116.7	123.2	123.7	116.0	124.0	123.2	116.6	124.1	116.0
6′	130.0	130.9	130.2	121.9	124.0	122.4	130.0	130.9	130.2	122.0	124.0	122.3	130.1	130.9	122.2	124.1
7′	144.9	145.6	144.9	145.2	145.9	145.3	145.0	145.6	145.0	145.3	146.0	145.4	144.8	145.7	145.2	146.1
8′	117.9	115.1	118.5	118.1	115.4	118.5	117.8	115.2	118.3	118.1	115.5	118.2	118.5	115.2	118.6	115.5
9′	168.0	167.6	166.6	168.0	167.6	166.7	167.9	167.4	166.4	168.0	167.4	166.5	166.6	167.4	166.7	167.4

[a] In acetone-d_6; asterisk (*) indicates 1:1 (v/v) D_2O–acetone-d_6. [b] Chemical shifts for the acetate and methoxyl carbons are in the Experimental section. [c] For numbering sequence, refer to formulas.

acetone-d_6 : D_2O) which confirms the work of Ishii and Hiroi[11] who found that the assignments given for these two carbons in previous studies were interchanged.

EXPERIMENTAL *

General.—Melting points are uncorrected. Evaporations were performed under reduced pressure at temperatures not exceeding 42° (unless otherwise stated). Optical rotations were obtained at 20° with a Perkin–Elmer model 141 polarimeter. NMR spectra were initially recorded with a Bruker AM-360 360 MHz wide-bore instrument fitted with a 5-mm probe and operated at 24–27°; and subsequently with a Bruker AMX-360 spectrometer. One- and two-dimensional NMR spectra were obtained using standard pulse-sequence programs. Chemical shifts (ppm) are relative to the central solvent peaks of acetone-d_6 (δ_C 29.8, δ_H 2.04 ppm), Me_2SO-d_6 (δ_C 39.5, δ_H 2.49 ppm), or $CDCl_3$ (δ_C 77.0, δ_H 7.24 ppm).

Thin-layer chromatography was performed with Alugram Sil-G/UV_{254} plates (Macherey–Nagel) with visualization either with UV light or by charring (5% H_2SO_4 in 95% EtOH). Preparative TLC was carried out with Kieselgel-60 on pre-coated plates (E. Merck) and column chromatography was with Kieselgel 60 (E. Merck) using a standard flash chromatography apparatus (Ace Glass). Solvent systems employed were as follows: *A*, 50:1 CCl_4–acetone; *B*, $CHCl_3$; *C*, 19:1 $CHCl_3$–EtOAc; D, 9:1 $CHCl_3$–EtOAc; *E*, EtOAc; *F*, 100:1 EtOAc–HOAc; *G*, 15:1 EtOAc–MeOH.

4-Acetoxycinnamoyl chlorides.—4-*O*-Acetylferulic acid and 4-*O*-acetylferuloyl chloride were prepared as previously reported[21]. *p*-Coumaric acid (25 g, 152 mmol) was acetylated in pyridine (45 mL) with acetic anhydride (40 mL, 424 mmol). The mixture was left for 4 h and quenched by pouring into ice–water (1 L) with stirring. A white precipitate that fell out during mixing was isolated by filtration, washed with H_2O, and air-dried. Crystallization from MeOH afforded 4-*O*-acetyl-*p*-coumaric acid (25.5 g, 81%): mp 205–211°; NMR (Me_2SO-d_6): δ_H 2.25 (Ac), 6.47 (d, 1 H, $J_{7,8}$ 16.0 Hz, H-8), 7.16 (m, 2 H, *J* 8.6 Hz, H-3,5), 7.58 (d, 1 H, H-7), 7.71 (m, 2 H, H-2,6); δ_C 20.9 (Ac), 119.4 (C-8), 122.4 (C-3,5), 129.5 (C-2,6), 132.1 (C-1), 143.1 (C-7), 152.0 (C-4), 167.7 (C-9), 169.1 (C=O).

The acid chlorides were prepared by refluxing a mixture of the 4-*O*-acetoxycinnamic acid (25 mmol) and thionyl chloride (4.5 mL, 3.8 equiv) in benzene (50 mL) for 45 min. The resulting clear solutions were evaporated to a solid, redissolved in toluene, and evaporated to a solid again. Crystallization from hot toluene gave the 4-acetoxycinnamoyl chlorides in 75–80% yields. 4-*O*-Acetyl-*p*-coumaroyl chloride: mp 118.5–121.5°; NMR (acetone-d_6): δ_H 2.28 (Ac), 6.87 (d, 1 H, $J_{7,8}$ 15.6 Hz, H-8),

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7.26 (m, 2 H, *J* 8.7 Hz, H-3,5), 7.87 (m, 2 H, H-2,6), 7.95 (d, 1 H, H-7); δ_C 21.0 (Ac), 122.8 (C-8), 123.4 (C-3,5), 131.5 (C-1,2,6), 150.9 (C-7), 154.7 (C-4), 166.1 (C-9), 169.2 (C=O).

*Methyl 2,3,4-tri-*O*-trimethylsilyl-β-*D*-galactopyranoside* (**2c**).—Methyl β-D-galactopyranoside (**2a**, 2.50 g, 12.9 mmol) was silylated with trimethylsilyl chloride (8 mL, 4.9 equiv) in pyridine (25 mL) for 5.5 h[25]. The mixture was diluted with toluene and evaporated to a syrupy solid. Addition and evaporation of toluene was repeated twice, and the resulting product was diluted with petroleum ether and filtered. The filtrate was evaporated to a syrup and placed under high vacuum (150 mtorr) for 1 h to provide 6.35 g of crude **2b**. The syrupy material was diluted with MeOH (100 mL), and to this solution was added (with stirring) methanolic K_2CO_3 (3 mL, 4.48 mg/mL)[18]. The mixture was left for 90 min at which time TLC indicated complete disappearance of the starting material. The solution was neutralized with HOAc (5 mL, 2.8 mg/mL MeOH) and evaporated to a syrup. Purification with silica gel chromatography (40 g, solvent *D*) provided **2c** (4.88 g, 92% based on **2a**) which crystallized from the syrup: mp 128.5–130° $[\alpha]_D$ −8.2° (*c* 1.97, acetone); lit.[19] mp 130.5–132°, $[\alpha]_D$ −1.72° (*c* 10.25, $CHCl_3$); NMR ($CDCl_3$): δ_H 0.095 and 0.13 ($SiCH_3$), 3.39 (dd, 1 H, $J_{3,4}$ 2.7 Hz, $J_{3,2}$ 9.3 Hz, H-3), 3.45 (ddd, 1 H, $J_{5,4}$ 0.9 Hz, $J_{5,6a}$ 4.5 Hz, $J_{5,6b}$ 7.4 Hz, H-5), 3.48 (s, 3 H, OCH_3), 3.57–3.64 (m, 1 H, H-6a), 3.61 (dd, 1 H, $J_{2,1}$ 7.5 Hz, H-2), 3.74 (dd, 1 H, H-4), 3.83 (ddd, 1 H, *J* 2.6 Hz, J_{gem} 11.2 Hz, H-6b), 4.08 (d, 1 H, H-1); δ_C 0.39, 0.57, and 0.61 ($SiCH_3$), 57.2 (OCH_3) 62.7 (C-6), 72.0 (C-2), 72.3 (C-4), 75.0 (C-5), 75.1 (C-3), 105.1 (C-1).

*Methyl 2,3,4-tri-*O*-trimethylsilyl-β-*D*-glucopyranoside* (**1c**).—Compound **1c** was prepared as **2c**, with the yield being significantly lower (62% from **1a**): mp 72–73°; $[\alpha]_D$ −6.0° (*c* 1.4, acetone); lit.[20] mp 72°, $[\alpha]_D$ −8.6° (*c* 0.5, $CHCl_3$); NMR ($CDCl_3$): δ_H 0.95, 0.11 and 0.12 ($SiCH_3$), 3.23 (dd, 1 H, $J_{2,1}$ 7.6 Hz, $J_{2,3}$ 8.8 Hz, H-2), 3.19–3.25 (m, 1 H, H-5), 3.39–3.42 (m, 2 H, H-3,4), 3.44 (OCH_3), 3.62 (ddd, 1 H, *J* 5.3 and 7.1 Hz, J_{gem} 11.7 Hz, H-6a), 3.77 (ddd, 1 H, *J* 2.8 and 6.3 Hz, H-6b), 4.08 (d, 1 H, H-1); δ_C 0.82, 1.01 and 1.29 ($SiCH_3$), 56.8 (OCH_3), 62.0 (C-6), 71.5 (C-4), 76.0 (C-2,5), 78.3 (C-3), 104.4 (C-1).

*Methyl 6-*O*-(4′-*O*-acetylferuloyl)-β-*D*-galactopyranoside* (**2g**).—Compound **2c** (2.03 g, 4.94 mmol) was dissolved in pyridine (25 mL), and 4-*O*-acetylferuloyl chloride (1.37 g, 1.09 equiv) was added with stirring. After 5 h the crude silylated reaction product was diluted with toluene and evaporated to a syrupy solid. The mixture was diluted with petroleum ether and filtered. The filtrate was evaporated to a syrup and diluted with 75% aq EtOH (30 mL) and left unstirred in the dark until *O*-desilylation was complete (3 days). Processing and subsequent crystallization from EtOH gave **2g** as white needles (1.85 g, 91%): mp 194.5–195.5°; $[\alpha]_D$ 9.4° (*c* 0.98, acetone–H_2O); NMR [1:1 (v/v) D_2O–acetone-d_6]: δ_H 2.19 (Ac), 3.41 (OCH_3), 3.46 (dd, 1 H, $J_{2,1}$ 7.7 Hz, $J_{2,3}$ 9.8 Hz, H-2), 3.54 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3), 3.75 (OCH_3), 3.78–3.82 (m, 1 H, H-5), 3.88 (dd, 1 H, $J_{4,5}$ 1.1 Hz, H-4), 4.18 (d, 1 H, H-1), 4.27 (dd, 1 H, $J_{6a,5}$ 4.6 Hz, J_{gem} 11.6 Hz, H-6a), 4.34 (dd, 1 H, $J_{6b,5}$ 7.7 Hz, H-6b), 6.46 (d, 1 H, $J_{8',7'}$ 16.0 Hz, H-8′), 7.02 (d, 1 H, $J_{5',6'}$ 8.1 Hz, H-5′),

7.14 (dd, 1 H, $J_{6',2'}$ 1.8 Hz, H-6'), 7.25 (d, 1 H, H-2'), 7.57 (d, 1 H, H-7'); δ_C 20.2 (OAc); 56.2, 57.0 (OCH_3).

Anal. Calcd for $C_{19}H_{24}O_{10}$: C, 55.34; H, 5.87. Found: C, 55.11; H, 5.92.

*Methyl 6-O-(4'-O-acetyl-*p*-coumaroyl)-β-*D*-galactopyranoside* (**2f**).—Compound **2f** was prepared according to the procedure for **2g** with the use of 4-*O*-acetyl-*p*-coumaroyl chloride to afford **2f** in 90% yield, which crystallized from absolute EtOH as white needles: mp 125–132°; $[\alpha]_D$ 9.8° (*c* 1.02, acetone–H_2O); NMR [1:1 (v/v) D_2O–acetone-d_6]: δ_H 2.19 (Ac), 3.41 (OCH_3), 3.46 (dd, 1 H, $J_{2,1}$ 7.6 Hz, $J_{2,3}$ 9.8 Hz, H-2), 3.55 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3), 3.78–3.82 (m, 1 H, H-5), 3.88 (dd, 1 H, $J_{4,5}$ 1.1 Hz, H-4), 4.18 (d, 1 H, H-1), 4.27 (dd, 1 H, $J_{6a,5}$ 4.6 Hz, J_{gem} 11.6 Hz, H-6a), 4.33 (dd, 1 H, $J_{6b,5}$ 7.7 Hz, H-6b), 6.42 (d, 1 H, $J_{8',7'}$ 16.0 Hz, H-8'), 7.04–7.07 (m, 2 H, H-3',5'), 7.53–7.60 (m, 3 H, H-2', 6', 7'); δ_C 20.7 (Ac); 57.0 (OCH_3).

Anal. Calcd for $C_{18}H_{22}O_9$: C, 56.54; H 5.80. Found: C, 56.58; H, 5.76.

Methyl6-O-(4'-O-acetyl p*-coumaroyl)-β-*D*-glucopyranoside* (**1f**).—Coupling procedures were as for **2g**. Purification by silica gel chromatography (40 g, solvent *E*, 200 mL), followed by solvent *G* (9200 mL)), and subsequent crystallization gave **1f** (82%): mp 160–164°; $[\alpha]_D$ −14.5° (*c* 1.2, acetone–H_2O); NMR [1:1 (v/v) D_2O–acetone-d_6]: δ_H 2.20 (Ac), 3.18 (dd, 1 H, $J_{2,1}$ 8.0 Hz, $J_{2,3}$ 9.1 Hz, H-2), 3.35–3.45 (m, 5 H, OCH_3, H-3, 4), 3.54–3.59 (m, 1 H, H-5), 4.24 (d, 1 H, H-1), 4.28 (dd, 1 H, $J_{6a,5}$ 5.9 Hz, J_{gem} 12.1 Hz, H-6a), 4.43–4.46 (m, 2.5 H, $J_{6b,5}$ 2.2 Hz, HDO and H-6b), 6.44 (d, 1 H, $J_{8',7'}$ 16.1 Hz, H-8'), 7.05–7.09 (m, 2 H, H-3',5'), 7.56–7.61 (m, 3 H, H-2', 6',); δ_C 20.7 (Ac); 57.0 (OCH_3).

Anal. Calcd for $C_{19}H_{24}O_{10}$: C, 56.54; H, 5.80. Found: C, 56.57; H, 5.76.

*Methyl 6-O-(4'-O-acetylferuloyl)-β-*D*-glucopyranoside* (**1g**).—The same procedure employed for **2g** was used. Purification with silica gel chromatography (40 g, solvent *E*) and subsequent crystallization from 95% EtOH gave **1g** (83%) as small hygroscopic white needles: mp 127.5–129.5°; $[\alpha]_D$ −16.6° (*c* 0.92, acetone–H_2O); NMR [1:1 (v/v) D_2O–acetone-d_6]: δ_H 2.19 (Ac), 3.18 (dd, 1 H, $J_{2,1}$ 8.0 Hz, $J_{2,3}$ 9.1 Hz, H-2), 3.34–3.45 (m, 5 H, H-3, 4, OCH_3), 3.54–3.59 (m, 1 H, H-5), 3.75 (OCH_3), 4.24 (d, 1 H, H-1), 4.28 (dd, 1 H, $J_{6a,5}$ 5.8 Hz, J_{gem} 12.1 Hz, H-6a), 4.44 (dd, 1 H, $J_{6b',5'}$ 2.2 Hz, H-6b), 6.48 (d, 1 H, $J_{8',7'}$ 16.0 Hz, H-8'), 7.02 (d, 1 H, $J_{5',6'}$ 8.2 Hz, H-5'), 7.14 (dd, 1 H,. $J_{6',2'}$ 1.9 Hz, H-6'), 7.26 (d, 1 H, H-2'), 7.57 (d, 1 H, H-7'); δ_C 20.2 (Ac) 56.2, 57.0 (OCH_3).

Anal. Calcd for $C_{17}H_{22}O_9$: C, 55.34; H, 5.87. Found: C, 55.21; H, 5.93.

Deacetylations.—The acetylated derivative (500 mg) was suspended in 95% EtOH (5 mL), and pyrrolidine (250 μL) was added (which caused the solution to turn yellow). The starting material typically dissolved within 15 min and the reaction was allowed to continue for a total of 1 h. The mixture was added directly to a column of strongly acidic ion-exchange resin [Amberlite IRA-120 (H^+), 40 mL, washed and packed in 95% EtOH]. Collection of the appropriate fractions provided the deprotected esters.

*Methyl 6-O-(*p*-coumaroyl)-β-*D*-galactopyranoside* (**2h**).—The material obtained

from the ion-exchange column could be crystallized from hot H_2O to give **2h** as off-white needles (407 mg, 90%): mp 103.5–106.5; $[\alpha]_D$ 14.7° (*c* 1.09, acetone–H_2O); NMR (9:1 acetone-d_6–D_2O): δ_H 3.43 (OCH_3); 3.50–3.59 (m, 2 H, H-2, 3); 3.79 (ddd, 1 H, $J_{5,4}$ 1.2 Hz, $J_{5,6a}$ 4.9 Hz, $J_{5,6b}$ 7.4 Hz, H-5); 3.90 (dd, 1 H, $J_{4,3}$ 3.1 Hz, H-4); 4.18 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1); 4.29 (dd, 1 H, J_{gem} 11.5 Hz, H-6a); 4.35 (dd, 1 H, H-6b) 6.30 (d, 1 H, $J_{8',7'}$ 16.0 Hz, H-8'); 6.83 (m, 2 H, H-3', 5'); 7.45 (m, 2 H, H-2', 6'); 7.57 (d, 1 H, H-7'); δ_C (acetone-d_6), 56.6 (OCH_3).

Anal. Calcd for $C_{16}H_{20}O_8$: C, 56.47; H 5.92. Found: C, 56.39; H, 5.95.

Methyl 6-O-feruloyl-β-D-galactopyranoside (**2i**).—The fractions collected from the ion-exchange column were processed to afford **2i** as a white foam (461 mg, 95%): $[\alpha]_D$ 14.1° (*c* 0.75, acetone–H_2O); NMR (9:1 acetone-d_6–D_2O), δ_H 3.43 (OCH_3); 3.48–3.59 (m, 2 H, H-2, 3); 3.79 (m, 1 H, H-5); 3.85 (OCH_3); 3.90 (dd, 1 H, $J_{4,5}$ 1.2 Hz, $J_{4,3}$ 3.0 Hz, H-4); 4.18 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1); 4.31 (dd, 1 H, $J_{6a,5}$ 5.0 Hz, J_{gem} 11.4 Hz, H-6a); 4.37 dd, 1 H, $J_{6b,5}$ 7.3 Hz, H-6b); 6.37 (d, 1 H, $J_{8',7'}$ 15.9 Hz, H-8'); 6.84 (d, 1 H, $J_{5',6'}$ 15.9 Hz, H-8'); 6.84 (d, 1 H, $J_{5',6'}$ 8.2 Hz, H-5'); 7.08 (dd, 1 H, $J_{2',6'}$ 1.9 Hz, H-6'); 7.24 (d, 1 H, H-2'); 7.58 (d, 1 H, H-7'); δ_C (acetone-d_6), 56.3, 56.6 (OCH_3).

Anal. Calcd for $C_{17}H_{22}O_9$: C, 55.13; H, 5.99. Found: C, 54.98; H, 6.03.

*Methyl 6-O-(*p*-coumaroyl)-β-D-glucopyranoside* (**1h**).—The appropriate fractions from the ion-exchange column were processed to afford **1h** as a white foam (425 mg, 94%): $[\alpha]_D$ −18.1° (*c* 1.0, acetone–H_2O); NMR (9:1 acetone-d_6–D_2O): δ_H 3.20 (dd, 1 H, $J_{2,1}$ 7.8 Hz, $J_{2,3}$ 9.0 Hz, H-2); 3.35–3.47 (m, 2 H, H-3, 4); 3.41 (OCH_3); 3.55 (m, 1 H, H-5); 4.22 (d, 1 H, H-1); 4.28 (dd, 1 H, $J_{6a,5}$ 6.1 Hz, J_{gem} 11.9 Hz, H-6a); 4.47 (dd, 1 H, $J_{6b,5}$ 2.1 Hz, H-6b); 6.34 (d, 1 H, $J_{8',7'}$ 16.0 Hz, H-8'); 6.85 (m, 2 H, H-3', 5'); 7.49 (m, 2 H, H-2', 6'), 7.60 (d, 1 H, H-7'); δ_C (acetone-d_6), 56.7 (OCH_3).

Anal. Calcd for $C_{16}H_{20}O_8$: C, 56.47; H, 5.92. Found: C, 56.30; H, 6.02.

Methyl 6-O-feruloyl-β-D-glucopyranoside (**1i**).—Processing of the appropriate fractions from the ion-exchange column gave **1i** as a white foam (392 mg, 90%): $[\alpha]_D$ −16.9° (*c* 1.47, acetone–H_2O); NMR (9:1 acetone-d_6–D_2O): δ_H 3.21 (dd, 1 H, $J_{2,1}$ 7.8 Hz, $J_{2,3}$ 9.0 Hz, H-2); 3.36–3.49 (m, 5 H, OCH_3, H-3, 4); 3.56 (ddd, 1 H, $J_{5,6b}$ 2.1, $J_{5,6a}$ 6.0 Hz, $J_{5,4}$ 9.5 Hz, H-5); 3.85 (OCH_3); 4.23 (d, 1 H, H-1); 4.30 (dd, 1 H, J_{gem} 12.0 Hz, H-6a); 4.47 (dd, 1 H, H-6b); 6.39 (d, 1 H, $J_{8',7'}$ 15.9 Hz, H-8'); 6.84 (d, 1 H, $J_{5',6'}$ 8.2 Hz, H-5'); 7.08 (dd, 1 H, $J_{6',2'}$ 2.0 Hz, H-6'); 7.26 (d, 1 H, H-2'); 7.59 (d, 1 H, H-7'); δ_C (acetone-d_6), 56.3, 56.7 (OCH_3).

Anal. Calcd for $C_{17}H_{22}O_9$: C, 55.13; H, 5.99. Found: C, 55.03; H, 6.05.

Acetylations.—The crystalline 4'-acetoxycinnamates (**1f** and **g**, and **2f** and **g**; 200 mg) were dissolved in pyridine (2 mL) and acetic anhydride (1.5 mL) and left overnight. The reaction was quenched with 95% EtOH, diluted with toluene, and evaporated to a syrup. The syrup was diluted with CH_2Cl_2 and washed successively with 3% HCl, H_2O, and aq $NaHCO_3$. Standard processing gave the fully acetylated materials described below.

*Methyl 2,3,4-tri-O-acetyl-6-O-(4'-O-acetyl-*p*-coumaroyl)-β-D-glucopyranoside* (**1j**).

Compound **1j** crystallized from 95% EtOH as small white needles: mp 158.5–160°; $[\alpha]_D$ 11.5° (*c* 1.86, acetone); NMR (acetone-d_6): δ_H 1.93, 1.98, 2.00 and 2.27 (Ac), 3.46 (OCH_3), 4.01 (dt, 1 H, $J_{5,4}$ 10.0 Hz, $J_{5,6a}+J_{5,6b}$ 7.6 Hz, H-5), 4.34 (m, 2 H, H-6a, 6b), 4.67 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.92 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2), 5.09 (t, 1 H, $J_{4,3}+J_{4,5}$ 19.4 Hz, H-4), 5.26 (t, 1 H, $J_{3,2}+J_{3,4}$ 19.1 Hz, H-3), 6.56 (d, 1 H, $J_{7',8'}$ 16.0 Hz, H-7'), 7.20 (m, 2 H, H-3',5'), 7.71 (d, 1 H, H-8'), 7.74 (m, 2 H, H-2',6'); δ_C 20.5, 20.5, 20.6 and 20.9 (Ac), 56.8 (OCH_3), 169.4, 169.6, 170.0, 170.3 (C=O).

Anal. Calcd for $C_{24}H_{28}O_{12}$: C, 56.69; H, 5.55. Found: C, 56.71; H, 5.57.

*Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(4'-*O*-acetylferuloyl)-β-*D*-glucopyranoside* (**1k**). Compound **1k** crystallized from 95% EtOH as small white needles: mp 152–153°; $[\alpha]_D$ 12.6° (*c* 1.51, acetone); NMR (acetone-d_6): δ_H 1.94, 1.99, 2.00 and 2.25 (Ac); 3.46 and 3.89 (OCH_3); 4.00 (m, 1 H, $J_{5,4}$ 10.0 Hz, H-5), 4.32 (m, 1 H, $J_{6a,5}$ 5.0 Hz, J_{gem} 12.3 Hz, H-6a), 4.36 (m, 1 H, $J_{6b,5}$ 2.5 Hz, H-6b), 4.66 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.92 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2), 5.09 (t, 1 H, $J_{4,3}+J_{4,5}$ 19.4 Hz, H-4), 5.26 (t, 1 H, $J_{3,2}+J_{3,4}$ 19.0 Hz, H-3), 6.60 (d, 1 H, $J_{8',7'}$ 16.0 Hz, H-8'), 7.11 (d, 1 H, $J_{5',6'}$ 8.1 Hz, H-5'), 7.25 (dd, 1 H, $J_{2',6'}$ 1.83 Hz, H-6'), 7.47 (d, 1 H, H-2'), 7.68 (d, 1 H, H-7'); δ_C 20.4, 20.5, 20.5 and 20.6 (Ac); 56.4 and 56.8 (OCH_3); 168.8, 169.6, 169.9 and 170.3 (C=O).

Anal. Calcd for $C_{25}H_{30}O_{13}$: C, 55.76; H 5.62. Found: C, 55.84; H, 5.61.

*Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(4'-*O*-acetyl-*p*-coumaroyl)-β-*D*-galactopyranoside* (**2j**). Compound **2j** was isolated as a clear syrup: $[\alpha]_D$ −27.4° (*c* 2.23, acetone); NMR: δ_H ($CDCl_3$) 1.95, 2.03, 2.13 and 2.27 (Ac), 3.49 (OCH_3), 3.96 (t, 1 H, $J_{5,6a}+J_{5,6b}$ 14.3 Hz, H-5), 4.18 (dd, 1 H, $J_{6a,5}$ 6.9 Hz, J_{gem} 11.3 Hz, H-6a), 4.36 (dd, 1 H, $J_{6b,5}$ 6.5 Hz, H-6b), 4.39 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 5.01 (dd, 1 H, $J_{3,4}$ 3.4 Hz, $J_{3,2}$ 10.5 Hz, H-3), 5.19 (dd, 1 H, H-2), 5.43 (d, 1 H, H-4), 6.32 (d, 1 H, $J_{7',8'}$ 16.0 Hz, H-8'), 7.09 (d, 2 H, *J* 8.6 Hz, H-3',5'), 7.50 (d, 2 H, H-2',6'), 7.63 (d, 1 H, H-7'); δ_C (acetone-d_6) 20.5, 20.5, 20.6, 20.9 (Ac), 56.7 (OCH_3), 169.4, 169.7, 170.2, 170.7 (C=O).

Anal. Calcd for $C_{24}H_{28}O_{12}$: C, 56.69; H, 5.55. Found: C, 56.61; H, 5.59.

*Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(4'-*O*-acetylferuloyl)-β-*D*-galactopyranoside* (**2k**). Compound **2k** was isolated as a clear syrup: $[\alpha]_D$ −27.0 (*c* 3.68, acetone); NMR (acetone-d_6): δ_H ($CDCl_3$) 1.95, 2.03, 2.14 and 2.28 (Ac); 3.49 and 3.83 (OCH_3); 3.95 (dt, 1 H, $J_{5,4}$ 1.1 Hz, $J_{5,6a}+J_{5,6b}$ 13.4 Hz, H-5), 4.18 (dd, 1 H, $J_{6a,5}$ 7.1 Hz, J_{gem} 11.2 Hz, H-6a), 4.37 (dd, 1 H, $J_{6b,5}$ 6.4 Hz, H-6b), 4.40 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 5.01 (dd, 1 H, $J_{3,4}$ 3.4 Hz, $J_{3,2}$ 10.5 Hz, H-3), 5.19 (dd, 1 H, H-2), 5.43 (dd, 1 H, H-4), 6.32 (d, 1 H, $J_{8',7'}$ 16.0 Hz, H-8'), 7.00–7.09 (m, 3 H, H-2', 5', 6'), 7.61 (d, 1 H, H-7'); δ_C 20.4, 20.4, 20.5 and 20.6 (Ac), 56.3 (Ar-OCH_3), 56.7 (OCH_3), 168.8, 169.7, 170.2 and 170.7 (C=O).

Anal. Calcd for $C_{25}H_{30}O_{13}$: C, 55.76; H, 5.62. Found: C, 55.81; H, 5.64 .

Procedure for TBDMS-acylation sequence.—The generation of methyl 2,3-di-*O*-acetyl-5-*O*-*tert*-butyldimethylsilyl-α-L-arabinofuranoside (**3c**) was followed by *O*-desilylation and subsequent coupling to the 4'-acetoxycinnamoyl chlorides. The peracetylated esters **3g** and **3h** were deacetylated in pyrrolidine–95% EtOH.

*Methyl 2,3-di-*O*-acetyl-5-*O*-tert-butyldimethylsilyl-α-*L*-arabinofuranoside* (**3c**). Methyl α-L-arabinofuranoside[21,26] (2.54 g, 15.5 mmol) was dissolved in pyridine (20 mL) under an N_2 atmosphere, and cooled in an ice–water bath. *tert*-Butyldimethylsilyl chloride (Petrarch, 2.44 g, 16.2 mmol) was added, the mixture was stirred for 5 min, and the flask was removed from the bath and left stirring overnight. Purification of the reaction mixture (silica gel chromatography) provided methyl 5-*O*-*tert*-butyldimethylsilyl-α-L-arabinofuranoside (**3b**) as a clear syrup in 89% yield: $[\alpha]_D$ −79.7° (*c* 2.68, acetone); NMR (acetone-d_6): δ_C 3.2 [$Si(CH_3)_2$], 18.8 [$C(CH_3)$], 26.2 [$C(CH_3)_3$], 54.7 (OCH_3), 64.2 (C-5), 78.5 (C-3), 82.5 (C-4), 85.5 (C-2), 110.1 (C-1).

Anal. Calcd for $C_{12}H_{26}O_5Si$: C, 51.77; H 9.41. Found: C, 51.75; H, 9.44.

The crude reaction mixture containing **3b** could be acetylated without purification, providing a one-pot procedure for the formation of **3c**. Acetic anhydride (6 mL, 4.1 equiv) was added to the crude solution of **3b**, and the mixture stirred for 5 h. The reaction mixture was quenched with 95% EtOH and diluted with CH_2Cl_2. The organic phase was washed subsequently with H_2O, 3% aq HCl, H_2O, and aq $NaHCO_3$. The organic layer was dried, filtered, and evaporated to a syrup. Two additions and evaporations of toluene eliminated the remaining pyridine. Purification by silica gel chromatography (40 g, solvent *A*) gave **3c** as a clear syrup (4.73 g, 84.3% from **3a**): $[\alpha]_D$ −66.1° (*c*, 1.08, acetone); NMR (acetone-d_6): δ_H 0.090, 0.096 [$Si(CH_3)_2$]; 0.92 [$C(CH_3)_3$]; 2.03, 2.04 (Ac); 3.33 (OCH_3); 3.84, 3.87 (s's, 2 × 1 H, H-5a, 5b); 4.04 (m, 1 H, H-4); 4.86 (bs, 1 H, H-1); 4.97 (bd, 1 H, $J_{2,3}$ 1.7 Hz, H-2); 5.08 (dd, 1 H, $J_{3,4}$ 5.1 Hz, H-3); δ_C 3.5 [$Si(CH_3)_2$]; 18.8 [$C(CH_3)$]; 20.7 (Ac); 26.2 [$C(CH_3)_3$]; 54.5 (OCH_3); 63.2 (C-5); 77.7 (C-3); 82.7 (C-4); 83.5 (C-2); 107.5 (C-1); 170.3, 170.3 (Ac).

Anal. Calcd for $C_{16}H_{30}O_7Si$: C, 53.01; H, 8.34. Found: C, 52.91; H, 8.48.

*Methyl 2,3-di-*O*-acetyl-α-*L*-arabinofuranoside* (**3d**). Syrupy **3c** (4.01 g, 11.05 mmol) was diluted with 80% HOAc (20 mL) and left for 24 h at room temperature. The product was evaporated to a syrup and diluted with CH_2Cl_2, which was subsequently washed twice with H_2O and once with aq $NaHCO_3$. Standard work-up gave **3d** (2.50 g, 91%) as a clear syrup: $[\alpha]_D$ −91.9° (*c* 1.18, acetone); NMR ($CDCl_3$): δ_H 2.06, 2.07 (Ac); 3.36 (OCH_3); 3.73–3.89 (m, 2 H, H-5a, 5b); 4.06 (m, 1 H, H-4); 4.88 (bs, 1 H, H-1); 4.99 (dd, 1 H, $J_{3,2}$ 1.6 Hz, $J_{3,4}$ 5.3 Hz, H-3); 5.05 (d, 1 H, H-2); δ_C 20.6, 20.7 (Ac); 54.7 (OCH_3); 61.9 (C-5), 77.1 (C-3); 81.6 (C-4); 82.8 (C-2); 106.5 (C-1); 169.7, 170.5 (C=O).

Anal. Calcd for $C_{10}H_{16}O_7$: C, 48.39; H, 6.50. Found: C, 48.26; H, 6.53.

Crude **3c**, obtained without silica gel chromatography, can also be subjected to the *O*-desilylation reaction to provide **3d** in 70% overall yield (based on **3a**).

*Methyl 2,3-di-*O*-acetyl-5-*O*-(4′-*O*-acetyl* p*-coumaroyl)-α-*L*-arabinofuranoside* (**3e**). A mixture of **3d** (818 mg, 3.3 mmol) and 4′-acetoxy-*p*-coumaroyl chloride (806 mg, 3.59 mmol) in pyridine (5 mL) was stirred for 5 h. The mixture was diluted with toluene and evaporated to a syrup. Purification by silica gel chromatography (40 g, solvent *B*) gave **3e** (1.20 g, 84%) as a clear viscous syrup: $[\alpha]_D$ −65.4° (*c* 2.68

acetone); NMR (acetone-d_6): δ_H 2.06 (Ac), 2.26 (Ac), 3.35 (OCH_3), 4.30 (dt, 1 H, $J_{4,5a}$ 3.3 Hz, $J_{4,3}+J_{4,5b}$ 10.7 Hz, H-4), 4.37 (dd, 1 H, $J_{5a,4}$ 5.5 Hz, J_{gem} 11.8 Hz, H-5a), 4.55 (dd, 1 H, H-5b), 4.94 (s, 1 H, H-1), 5.03 (d, 1 H, $J_{2,3}$ 1.6 Hz, H-2), 5.07 (ddd, 1 H, $J_{3,1}$ 0.7 Hz, $J_{3,4}$ 5.2 Hz, H-3), 6.55 (d, 1 H, $J_{8',7'}$ 16.1 Hz, H-8'), 7.18–7.20 (m, 2 H, H-3', 5'), 7.70–7.74 (m, 3 H, H-2', 6', 7'); δ_C 20.6, 20.7, 20.9 (Ac); 54.8 (OCH_3); 169.4, 170.1, 170.6, (Ac).

Anal. Calcd for $C_{21}H_{24}O_{10}$: C, 57.8; H, 5.54. Found: C, 58.06; H, 5.60.

Methyl 2,3-di-O-acetyl-5-O-(4'-O-acetylferuloyl)-α-L-arabinofuranoside (**3f**). Compound **3f** was prepared as described for **3e** in 89% yield: $[\alpha]_D$ −53.5° (*c* 1.53, acetone); NMR (acetone-d_6): δ_H 2.06, 2.07, 2.24 (OAc); 3.35, 3.89 (OCH_3); 4.28 (m, 1 H, H-4); 4.34 (dd, 1 H, $J_{5a,4}$ 5.5 Hz, J_{gem} 11.8 Hz, H-5a); 4.54 (dd, 1 H, $J_{5b,4}$ 3.2 Hz, H-5b); 4.93 (bs, 1 H, H-1); 5.02 (bd, 1 H, $J_{2,3}$ 1.6 Hz, H-2); 5.05 (m, 1 H, $J_{3,4}$ 5.2 Hz, H-3); 6.60 (d, 1 H, $J_{8',7'}$ 16.0 Hz, H-8'); 7.11 (d, 1 H, $J_{5',6'}$ 8.1 Hz, H-5'); 7.27 (dd, 1 H, $J_{6',2'}$ 1.8 Hz, H-6'); 7.48 (d, 1 H, H-2'); 7.70 (d, 1 H, H-7'); δ_C 20.4, 20.6, 20.7 (Ac); 54.8, 56.3 (OCH_3); 168.8, 170.1, 170.6 (Ac).

Anal. Calcd for $C_{22}H_{26}O_{11}$: C, 56.65; H, 5.62. Found: C, 56.68; H, 5.69.

Methyl 5-O-(p-coumaroyl)-α-L-arabinofuranoside (**3g**). Syrupy **3e** (250 mg) was dissolved in 95% EtOH (5 mL). Pyrrolidine (500 μL) was added, and the mixture was left without stirring for 48 h. Neutralization and purification as described for the piperidine deacetylation reactions afforded **3g** (83%) as a clear syrup: $[\alpha]_D$ −89.0° (*c* 1.0, acetone); NMR (acetone-d_6): δ_H 3.31 (OCH_3), 3.96 (dd, 1 H, $J_{3,2}$ 3.7 Hz, $J_{3,4}$ 6.4 Hz, H-3), 4.06 (dd, 1 H, $J_{2,1}$ 1.6 Hz, H-2), 4.14 (dt, 1 H, $J_{4,5b}$ 3.6 Hz, $J_{4,5a}+J_{4,3}$ 12.5 Hz, H-4), 4.27 (dd, 1 H, J_{gem} 11.8 Hz, H-5a), 4.40 (dd, 1 H, H-5b), 4.80 (d, 1 H, H-1), 6.36 (d, 1 H, $J_{8',7'}$ 16.0 Hz, H-8'), 6.87–6.90 (m, 2 H, H-3', 5'), 7.51–7.54 (m, 2 H, H-2', 6'), 7.64 (d, 1 H, H-7'); δ_C 55.0 (OCH_3).

Anal. Calcd for $C_{15}H_{18}O_7$; C, 58.06; H, 5.85. Found: C, 57.93; H, 5.75.

Methyl 5-O-feruloyl-α-L-arabinofuranoside (**3h**). Compound **3h** was prepared as described for **3g** in 73% yield as a hygroscopic solid which can be crystallized from CH_2Cl_2 (ref. 21): mp 71–72°; $[\alpha]_D$ −73.8° (*c* 0.70, acetone).

Anal. Calcd for $C_{16}H_{20}O_8$: C, 56.47; H 5.92. Found: C, 56.38; H, 5.79.

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