Stereoselective Syntheses of α-Glucuronides Using Dehydrative Glycosylation

Shinkiti Koto,* Teruhisa Miura, Motoko Hirooka, Aya Tomaru, Mika Iida, Masanori Kanemitsu, Kazuhiro Takenaka, Shinichi Masuzawa, Saeko Miyaji, Naoko Kuroyanagi, Miki Yagishita, Shonosuke Zen, Kazuo Yago,†, # and Fumiya Tomonaga†

School of Pharmaceutical Sciences, Kitasato University, Shirokane, Minato-ku, Tokyo 108

†Department of Pharmacy, Kitasato University Hospital, Kitasato, Sagamihara 228

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Methyl and benzyl 2,3,4-tri-*O*-benzyl-D-glucopyranuronates, prepared from D-glucurono-6,3-lactone, afforded selectively the corresponding α-glucopyranosiduronates by the aid of the condensing reagent system composed of *p*-nitrobenzenesulfonyl chloride, silver trifluoromethanesulfonate, and triethylamine. Using this method, *O*-α-D-glucopyranuronosyl-(1→3)-*O*-α-L-arabinofuranosyl-(1→3)-D-xylopyranose, one of the minimal component units in the structure of plantago-mucilage A from the seeds of *Plantago asiatica* Linné constituting a Chinese medicine : chegianzi [車前子].

Dehydrative glycosylation[1] (Eq. 1), using a 1-OH sugar derivative as a glycosyl donor like 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**1**, DOH) and an acceptor (AOH), has an advantage over the glycosylations that need preparation and manipulation of reactive glycosyl donors.[2] The glycosylation reagent system (NST, Eq. 2)[3] composed of *p*-nitrobenzenesulfonyl chloride, silver trifluoromethanesulfonate, and triethylamine was usable for dehydrative glycosylation,[4] Using NST system, we have previously synthesized a highly branched tetrasaccharide.[5] The aim of this report is to show that NST is usable for the stereoselective α-glucopyranuronosylation using the 1-OH derivative of methyl and benzyl D-glucopyranuronates, **2**[6] and **3**(Chart 1).[7] No report of the synthesis of α-glucuronide by use of dehydrative glycosylation method has yet appeared.

$$\mathrm{DOH + AOH \rightarrow DOA + H_2O} \quad (1)$$

$$\mathrm{DOH + AOH + \textit{p}\text{-}NO_2C_6H_4SO_2Cl + CF_3SO_3Ag + Et_3N \rightarrow}$$
$$\mathrm{DOA + \textit{p}\text{-}NO_2C_6H_4SO_3H + AgCl + CF_3SO_3H\cdot Et_3N} \quad (2)$$

The donors **2** and **3** were prepared from the commercially available lactone **4**; this is an alternative to the known methods[6,7] which need oxidation processes.[8] The acetate **5**,[9] readily obtained form **4**, was conveniently reacted with moist acetyl bromide to give the bromide,[10] which was condensed with allyl alcohol in the presence of Ag_2CO_3. Treatment of the product **6** with methanolic sodium methoxide furnished the allyl β-glucuronide **7** (64% yield form **5**) (Chart 1). Mild benzylation[11] of **7** by use of benzyl bromide and NaH in dimethyl sulfoxide afforded the benzyl ether **8**. Hydrolysis and benzylation of **8** gave the benzyl ester **9**. The Rh-catalyzed deallylation[12] of **8** afforded **2** (35% from **7**). Efficient Pd-catalyzed deallylation[13] converted **9** into the fully benzylated donor **3** (36% form **7**). The 2-methoxyethyl group[14] was not suitable for preparing **3**. Treatment of the protected 2-methoxyethyl glucuronide **12** with $TiCl_4$ mainly afforded the isomerized product **13** instead of **3**, the hydrolyzate of the chloride **C** formed via the intermediate **B** (Chart 2).[14] Rapid isomerization proceeds presumably via the intermediate A, analogous to that postulated before.[14a]

The NST system performed the condensations of the donor **2** with four kinds of acceptors : **14**, **15**, **16**, and **17** (Chart 3) to afford the corresponding anomeric pairs of the cross-condensates in 82, 75, 89, and 86% yields, respectively (Table 1). Except for the case of the primary alcohol **17**, the α-glucuronides : **18**, **20**, and **22** were obtained mainly (Chart 4). Hydrogenolyses of the α-linked disaccharide derivatives, **18**, **20**, **22**, and **24** afforded the corresponding methyl esters **26**, **27**, **28**, and **29**. These esters were hydrolyzed to give the respective α-glucuronides **31**, **32**, **33**, and **34**. The structures of four (α-D-glucopyranosyluronic acid)-D-glucopyranoses, **31**, **32**, **33**, and **34**, and their methyl ester, **26**, **27**, **28**, and **29**, were confirmed by their ^{13}C NMR spectra in D_2O and the comparison with the data of the α-D-glucopyranosyluronic acids and the α-linked glucobioses[15] (Tables 2 and 3). By the NST system, the donor **3** condensed similarly with the above-mentioned four acceptors : **14**, **15**, **16**, and **17** (Table 1). The acceptors, **14**, **15**, and **16**, which are secondary alcohols, formed selectively the corresponding α-glucuronides **36**, **38**, and **40**. The primary alcohol **17** furnished a significant amount of the β-glucuronide **43**. Hydrogenolytical debenzylations of the totally benzylated glucuronide derivatives : **36**, **38**, **40**, and

Present address: Department of Pharmacy, Kitasato University East Hospital, Asamizodai, Sagamihara 228.

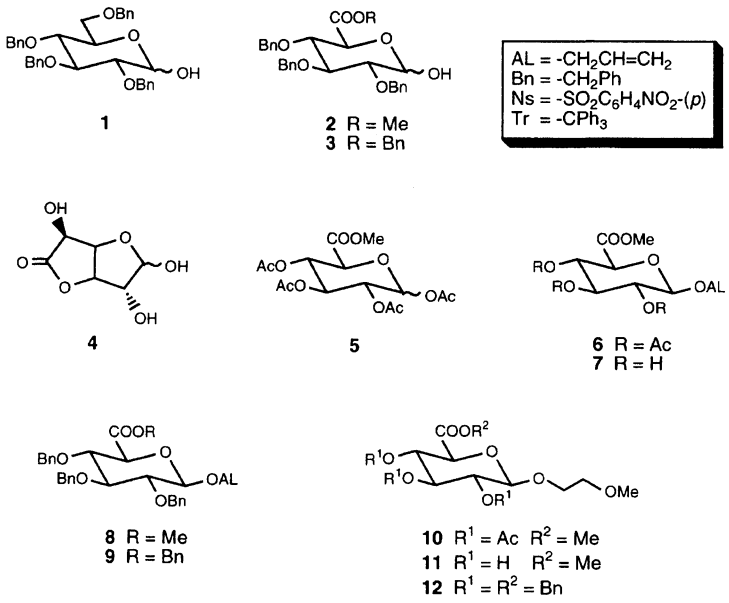


Chart 1.

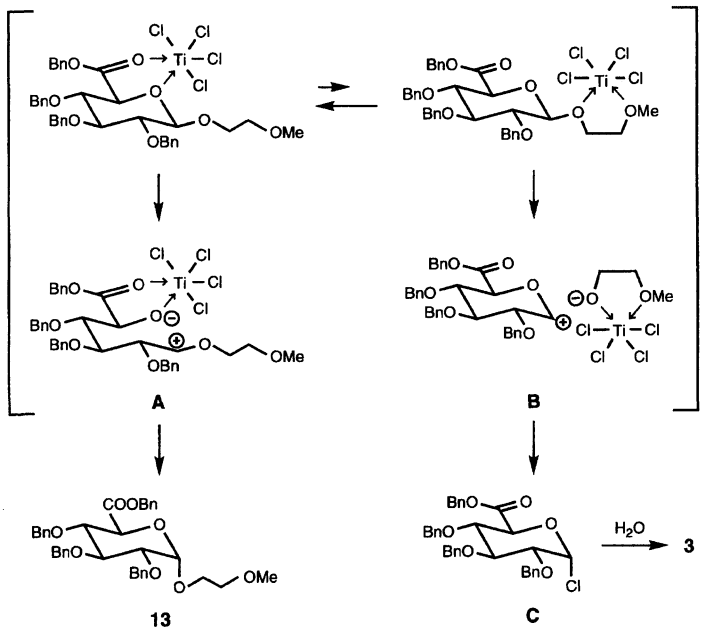


Chart 2.

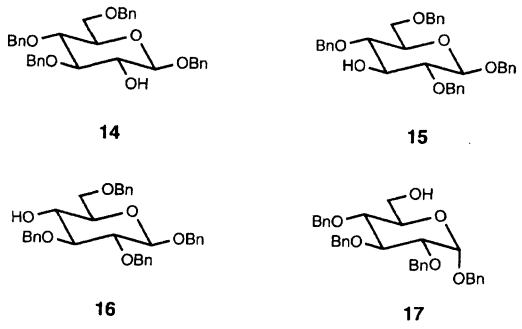


Chart 3.

42 gave the corresponding α-glucuronides **31**, **32**, **33**, and **34**. In general, glycosylation using a benzylated glucosyl donor and an appropriate promotor proceeds in α-selective manner.[2] Since the corresponding derivatives of methyl glucuronate also undergo α-selective glycosylation,[6a,8a] it seems that the influence of the carboxylic ester group on the stereochemical course of the reaction is not clear.[6a] However, we found that the donors **2** and **3** carried out α-selective condensation with secondary alcohols as acceptor by the NST system, whereas the similar condensation of **1** was not α-selective.[3,5] These results indicate that the ester group plays a role in the apparence of α-selectivity of the reaction. The ester group in the β-side of **2** and **3** may help the acceptor to enter into the anomeric center from the α-side of the interme-

Table 1. Results of Dehydrative Glycosylation (DOH+AOH→DOA)

DOH[a)]	AOH[a)]	Conditions[b)]	DOA % (α%)
2	**14**	A	**18+19** 82 (65)
2	**15**	A	**20+21** 75 (68)
2	**16**	A	**22+23** 89 (72)
2	**17**	B	**24+25** 86 (51)
3	**14**	A	**36+37** 80 (66)
3	**15**	A	**38+39** 77 (72)
3	**16**	A	**40+41** 90 (73)
3	**17**	B	**42+43** 83 (52)

a) DOH=donor hemiacetal, AOH=acceptor alcohol. b) A conditions, DOH : AOH : *p*-$NO_2C_6H_4SO_2Cl$: CF_3SO_3Ag : Et_3N (mol/mol)=1.3 : 1.0 : 2.5 : 2.5 : 2.5; B conditions, DOH : AOH : *p*-$NO_2C_6H_4SO_2Cl$: CF_3SO_3Ag : Et_3N (mol/mol) = 1.3 : 1.0 : 1.7 : 1.7 : 1.7.

diate **D**, whereas the intermediate **E** will give β-glucuronide (Chart 5). The NSDT system, composed of the NST and *N*,*N*-dimethylacetamide,[16] did not improve α-selectivity of the reaction at all. The ester group in **D** will prevent the amide from forming the β-imidate, the precursor of the α-glycosides.[16]

Knowing that the NST performs α-selective glucuronosylation, we planned to synthesize the trisaccharide **44** containing α-glucuronosyl linkage, using three monosaccharide units **3**, **45**, and **46** via the disaccharide derivative **47**, as shown in Fig. 1. The trisaccharide **44** is one of the minimal component units in the structure of plantago-mucilage A, a representative mucous polysaccharide from the seeds of *Plantago major* Linné. var. *asiatica* Decaisne (=*Plantago asiatica* Linné), which constitutes the Chinese medicine chegianzi [車前子].[17]

Mild benzylation[18] of the α-xyloside **48** using benzyl chloride and a limited amount of NaH gave a mixture of partially benzylated products, from which the desired 3-OH derivative **45** was obtained in 64% yield. Similarly, reaction of the acetate **50** with benzyl chloride and a limited amount of KOH afforded the 3-OH derivative **45** in 77% yield. Such benzylation was applied to the acetylated β-xyloside **51** to furnish mainly the 3-OH compound **52** (48%) (Chart 6). The structures of **45** and **52** were confirmed by the observation of the ^{1}H NMR spectra of their acetates. The spectra showed the presence of an acetoxyl group at the 3-position in each of them.

An excess amount of trityl chloride was allowed to react with the furanoside **53** to afford mainly the desired ditrityl ether **54** (48%) with minor amounts of the isomer **55** (31%).[19] Its structure was determined by the ^{1}H NMR spectrum of its acetate, which showed the presence of acetyl group at the 3-OH group in **54**. By way of allylation of the 3-OH group, **54** was converted into **57**, the precursor of the donor **46**.

The arabinofuranosylation of the acceptor **45** with the donor **46** using the NST and the related system[20] did not work in α-selective manner. However, the system composed of $CoBr_2$, bromotrimethylsilane, and tetrabutylammonium bromide[21] performed α-selective condensation to give **58** and **59** (59%, 88α%). The α-furanosyl structure of **58** was confirmed by the presence of the signal of C1′ at δ=106.5 in its ^{13}C NMR spectrum ($CDCl_3$).[20] This system was effective for the α-selective condensations of **46** and **52** to give **60** and **61** (48%, 85α%) (Chart 7). Similarly, the donor **62** was condensed with **45** and **52** to give **63** and **64** (49%, 88α%) and **65** and **66** (49%, 88α%), respectively. Hydrogenolysis of **63** gave the disaccharide **67**. The α-furanosyl linkage was confirmed by the observation of its ^{13}C NMR spectrum in D_2O; the signal of C1′ appeared at δ=111.6[15,20] (Table 4).

Pd-catalyzed deallylation[12] was applied to **58** to furnish the acceptor **47**, which was then condensed with **3** by the NST system to give the desired α-glucuronide **68** with the β-linked **69** (66%, 62α%). The signal of the newly formed C1″ with α-configuration was observed at δ=98.7 in the ^{13}C NMR spectrum ($CDCl_3$).[22] Hydrogenolytic debenzylation of **68** afforded the trisacchride **44**. The ^{13}C NMR spectrum (Table 4) measured in D_2O showed the signals of C1′ and C1″ at δ=111.9 and 102.4, respectively,[15] thereby showing that both of C1′ and C1″ have α-configuration.

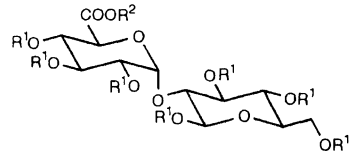
In conclusion, the NST system is conveniently usable for α-glucuronosylation using the 1-OH derivatives such as **2** and **3**.

Experimental

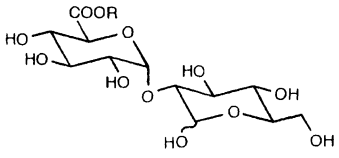
The solvent systems for column chromatography on silica gel (Kanto Chemical, No. 37047; gradient elution) and thin-layer chromatography on silica-gel plate (Merck DC-Plastikfolien Kieselgel 60 F254, Art. 5735) were chloroform–methanol (CM), 1,2-dichloroethane–ethyl acetate (DE), hexane–ethyl acetate (HE), isopropyl ether–ethyl acetate (IE), toluene–ethyl acetate (TE), and toluene–2-butanone (TK). Evaporation was carried out under reduced pressure. The optical rotations were measured on a JASCO DIP-150 Digital Polarimeter at room temp. The ^{1}H and ^{13}C NMR spectra were recorded with a Varian VXR-300 spectrometer, accompanied with the measurements of H,H-COSY, H,C-COSY, and DEPT spectra.[23]

The acetate **5**[9] was prepared from the lactone **4** available from Wako Pure Chemical Industries, Ltd. The acceptors, **14**,[24] **15**,[24] **16**,[25] and **17**,[26] were prepared by the known methods. The arabinosyl donor **62** was the product of Pfanstiehl Laboratory Inc.

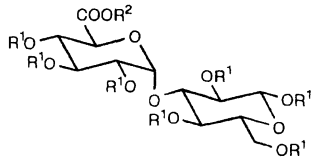
Methyl (Allyl 2,3,4-Tri-*O*-acetyl-β-D-glucopyranosid)uronate (6). To a cooled mixture of the acetate **5**[9] (5.767 g, 15.3 mmol), chloroform (170 ml), and acetyl bromide (34.6 ml), cold H_2O (6.9 ml) was added dropwise under good stirring. After evolution of HBr ceased, the vessel was tightly stoppered and kept in a refrigerator overnight. The mixture was concentrated under reduced pressure, and volatile matters were co-evaporated with toluene to give the aceto bromide. To this were added cold allyl alcohol (55 ml) and



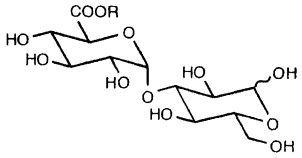
18 R^1 = Bn R^2 = Me (β-Anomer **19**)
36 R^1 = R^2 = Bn (β-Anomer **37**)



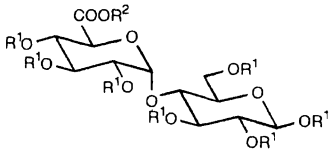
26 R = Me
31 R = H



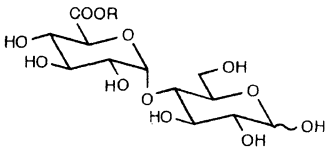
20 R^1 = Bn R^2 = Me (β-Anomer **21**)
38 R^1 = R^2 = Bn (β-Anomer **39**)



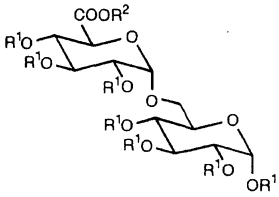
27 R = Me
32 R = H



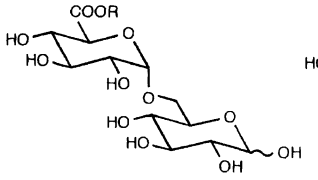
22 R^1 = Bn R^2 = Me (β-Anomer **23**)
40 R^1 = R^2 = Bn (β-Anomer **41**)



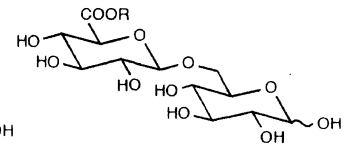
28 R = Me
33 R = H



24 R^1 = Bn R^2 = Me (β-Anomer **25**)
42 R^1 = R^2 = Bn (β-Anomer **43**)



29 R = Me
34 R = H



30 R = Me
35 R = H

Chart 4.

Ag_2CO_3 (12.7 g), and the mixture was shaken until most of the bromide was dissolved under cooling. The resulting slurry was stirred at room temp in the dark overnight. Filtration, evaporation, and chromatography with TK system gave **6** (4.303 g, 76%), mp 126—127 °C; $[\alpha]_D$ −30° (*c* 0.8, $CHCl_3$) (lit,[27] mp 133—134 °C; $[\alpha]_D$ −32° (*c* 1.1, $CHCl_3$)); ^{1}H NMR ($CDCl_3$) δ=4.60 (1H, d, $J_{1,2}$=7.5 Hz, H1), 5.03 (1H, dd, $J_{2,3}$=9.5 Hz, H2), 5.25 (1H, t, $J_{3,4}$=9.5 Hz, H3), 5.22 (1H, t, $J_{4,5}$=9.5 Hz, H4), 4.02 (1H, d, H5), 2.01 (3H, s, Ac), 2.03 (6H, s, 2Ac), 3.75 (3H, s, Me), 5.82 (1H, m, allyl); ^{13}C NMR ($CDCl_3$) δ=99.5 (C1), 71.2 (C2), 72.1 (C3), 69.4 (C4), 72.6 (C5), 167.2 (C6), 52.9 (Me), 117.8, 133.1 (allyl), 20.5, 20.5[7], 20.6[0] (Ac).

Found: C, 51.39; H, 5.97%. Calcd for $C_{16}H_{22}O_{10}$: C, 51.33; H, 5.93%.

Methyl (Allyl β-D-Glucopyranosid)uronate (7). Treatment of **6** (2.000 g, 5.3 mmol) with methanolic sodium methoxide (0.06%, 70 ml) at room temp for 1.5 h gave a yellowish solution, which was neutralized with acetic acid. The solvent was removed and the resulting residue was chromatographed with CM system to afford **7** (1.103 g, 84%), mp 73—74 °C; $[\alpha]_D$ −63° (*c* 0.8, H_2O); ^{1}H NMR (D_2O) δ=4.49 (1H, d, $J_{1,2}$=7.5 Hz, H1), 3.26 (1H, dd, $J_{2,3}$=9.0 Hz, H2), 3.44 (1H, t, $J_{3,4}$=9.0 Hz, H3), 3.51 (1H, quasi t, $J_{4,5}$=9.5 Hz, H4), 3.98 (1H, d, H5), 3.74 (3H, s, Me), 5.87 (1H, m, allyl); ^{13}C NMR (D_2O)[28] δ=105.9 (C1), 77.3 (C2), 79.8 (C3), 75.8 (C4), 79.1 (C5), 175.4 (C6), 57.7 (Me), 75.5, 123.5, 137.7 (allyl).

Found: C, 48.38; H, 6.57%. Calcd for $C_{10}H_{16}O_7$: C, 48.39; H, 6.50%.

Methyl (Allyl 2,3,4-Tri-*O*-benzyl-β-D-glucopyranosid)uronate (8). To a well-stirred mixture of **7** (1.086 g, 4.4 mmol), dimethyl sulfoxide (11 ml), and benzyl bromide (3.76 ml), was added NaH (ca. 60% dispersion in oil, 1.27 g) at 15 °C (bath temp). After stirring for 10 min, the solidified mixture was kept standing at 20 °C (bath temp) for 15 min. Toluene (165 ml) and H_2O (55 ml) were cautiously added, and the organic layer was washed with aq acetic acid (10%) and H_2O. After evaporation, chromatography with TK system gave **8** (1.26 g, 60%), mp 111—112 °C; $[\alpha]_D$ −5° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.51 (1H, d, $J_{1,2}$=7.5 Hz, H1), 3.52 (1H, dd, $J_{2,3}$=9.0 Hz, H2), 3.67 (1H, t, $J_{3,4}$=9.0 Hz, H3),

Table 2. ^{13}C NMR Spectral Data of Glucuronates (75.5 MHz, in D_2O)[a)]

C	26		27		28		29		30	
	α	β	α	β	α	β	α	β	α	β
1	92.1	98.7	94.9	98.7	94.5	98.4	94.8	98.7	95.5	99.3
2	79.3	81.6	72.6	75.3	74.0	76.7	74.1	76.7	74.8	77.4
3	73.9	76.8	82.3	84.5	75.8	78.8	75.6	78.6	75.9	79.0
4	72.4	72.5	72.6[7]	72.7[0]	79.4	79.2	72.3	72.1	72.7[6]	72.8[2]
5	73.7	78.4	73.7[8]	78.3	72.3	76.9	72.6	76.9	73.8	78.2
6	63.2	63.4	63.0	63.1	63.1	63.2	69.2	69.0	72.3	72.4
1′	99.6	100.7	101.9	101.8	102.2	102.1	101.0	100.9	106.2	106.2
2′	73.6	73.6	73.8[2]	73.8[2]	73.7[3]	73.7[0]	73.6	73.6	76.1	76.1
3′	74.9[8]	75.0[2]	75.1	75.1	74.9	74.9	75.2	75.2	78.4	78.4
4′	74.0	74.0	74.0	74.0	73.8	73.8	73.9	73.9	74.6	74.6
5′	73.7	73.7	73.6	73.6	74.3	74.3	73.5	73.5	77.9	77.9
6′	174.5	174.6	175.2	175.2	174.1	174.2	174.3	174.3	174.3	174.2
Me	55.7	55.6	55.6	55.6	55.8	55.8	55.7	55.7	56.5	56.5

a) The carbons in the sugar moiety at the non-reducing end have prime number and those at the reducing end are numbered without prime.

Table 3. ^{13}C NMR Spectral Data of Glucuronides (75.5 MHz, in D_2O)[a)]

C	31		32		33		34		35	
	α	β	α	β	α	β	α	β	α	β
1	92.9	99.5	95.7	99.4	95.2	99.1	94.8	98.7	95.5	99.4
2	79.8	82.2	73.3[7]	76.1	74.6	77.3	74.0	76.7	74.8	77.4
3	74.7	77.7	83.0	85.2	76.5	79.5	75.7	78.6	76.0	79.0
4	73.1	73.2	73.4[2]	73.5	80.4	80.3	72.2	72.0	72.7[6]	72.8[3]
5	74.5	79.1	74.7	79.0	73.2	77.8	72.7	76.9	73.8	78.2
6	64.0	64.2	63.7	63.9	63.9	64.0	69.0	68.7	72.1	72.3
1′	100.1	101.2	102.5	102.3	103.0	102.9	100.8	100.7	105.9[4]	106.0[3]
2′	74.4	74.4	74.6	74.6	74.8	74.7	73.7	73.7	76.1	76.1
3′	75.9	75.9	75.9	75.9	75.9	75.9	75.3	75.3	78.6	78.6
4′	74.9	74.9	74.9	74.9	74.8	74.8	74.3	74.3	74.7	74.7
5′	74.5	74.5	74.6	74.6	75.6	75.6	73.9	73.9	78.1	78.1
6′	177.4[7]	177.5[0]	177.2	177.1	177.9	177.9	177.1	177.1	176.4	174.6

a) The carbons in the sugar moiety at the non-reducing end have prime number and those at the reducing end are numbered without prime.

3.84 (1H, quasi t, $J_{4,5}$=9.5 Hz, H4), 3.91 (1H, d, H5), 3.73 (3H, s, Me), 5.94 (1H, m, allyl); ^{13}C NMR ($CDCl_3$) δ=102.8 (C1), 81.8 (C2), 83.8 (C3), 79.3 (C4), 74.5 (C5), 169.0 (C6), 52.4 (Me), 117.6, 133.0 (allyl).

Found: C, 71.63; H, 6.61%. Calcd for $C_{31}H_{34}O_7$: C, 71.80; H, 6.61%.

Benzyl (Allyl 2,3,4-Tri-*O*-benzyl-β-D-glucopyranosid)uronate (9). A mixture of **8** (1.174 g, 2.34 mmol), aq NaOH (2.0%, 4.53 ml), and 1,2-dimethoxyethane (11.7 ml) was stirred at 25 °C overnight. After evaporation in vacuo at 35 °C, the obtained residue was stirred in dimethyl sulfoxide (17 ml) containing benzyl bromide (1.2 ml) at 15 °C for 30 min and then at 25 °C for 2.5 h. After the usual work-up, chromatography with HE system gave **9** (0.97 g, 72%), mp 58—59 °C; $[\alpha]_D$ −21 ° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ=4.52 (1H, d, $J_{1,2}$=7.5 Hz, H1), 3.54 (1H, dd, $J_{2,3}$=9.0 Hz, H2), 3.67 (1H, t, $J_{3,4}$=9.0 Hz, H3), 3.86 (1H, t, $J_{4,5}$=9.0 Hz, H4), 3.95 (1H, d, H5), 5.95 (1H, m, allyl); ^{13}C NMR ($CDCl_3$) δ=102.9 (C1), 81.7 (C2), 83.8 (C3), 79.3 (C4), 74.6 (C5), 168.4 (C6), 67.3

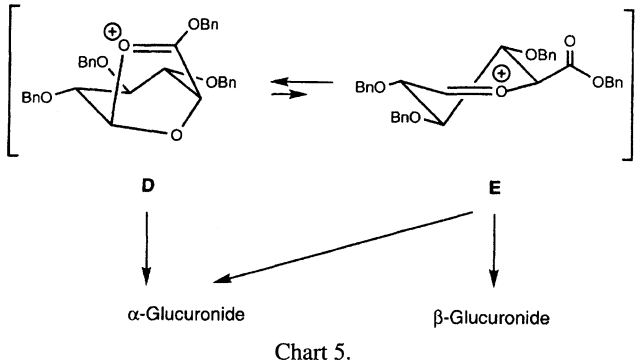


Chart 5.

(benzyl, ester), 117.6, 133.6 (allyl).

Found: C, 74.74; H, 6.42%. Calcd for $C_{37}H_{38}O_7$: C, 74. 73; H, 6.44%.

Methyl (2′-Methoxyethyl 2,3,4-Tri-*O*-acetyl-β-D-glucopyran-

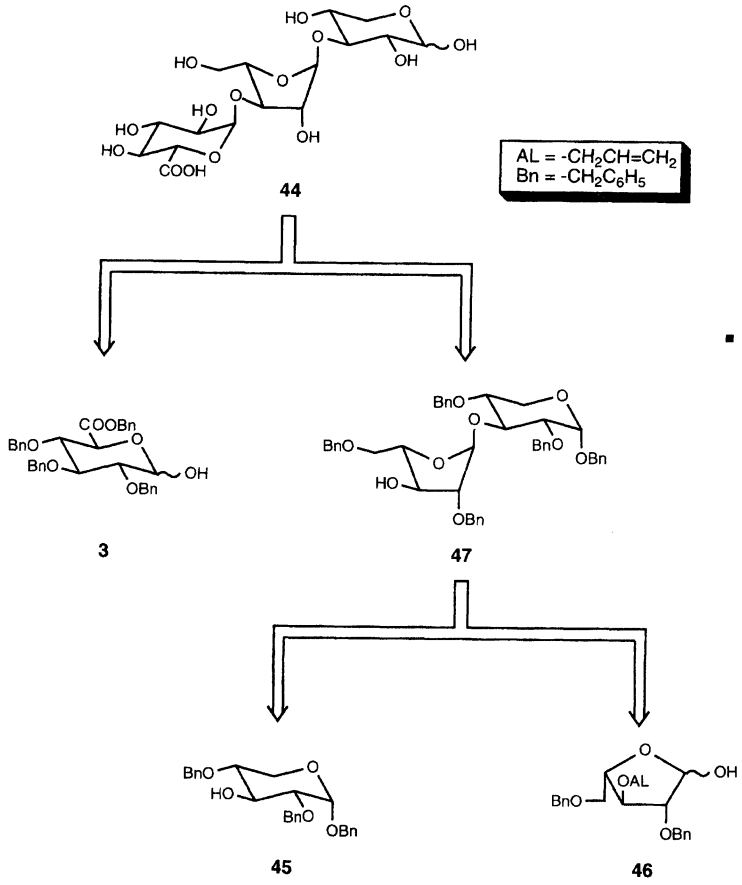


Fig. 1. Synthesis of α-D-GlcA*p*-(1→3)-α-L-Ara*f*-(1→3)-D-Xyl, a component of plantago-mucilage A from the seeds of *Plantago asatica* Linné constituing a Chinese medincine chegianzi [車前子].

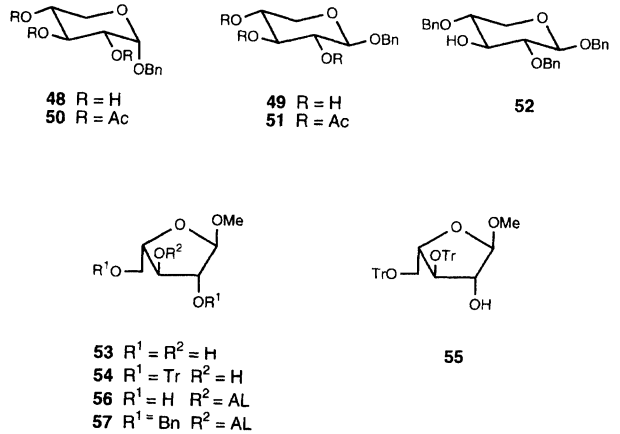


Chart 6.

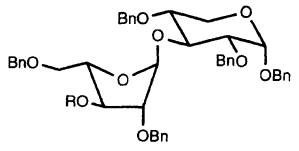
osid)uronate (10). A crude bromide, obtained from **5** (501 mg, 1.33 mmol) in a similar manner to that described for the preparation of **6**, was stirred in 2-methoxyethanol (11 ml) containing Ag_2CO_3 (1.1 g) at room temp overnight in the dark. Usual work-up and chromatography with TK system afforded **10** (377 mg, 72%), mp 90—100 °C; $[\alpha]_D$ −19° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.66 (1H, d, $J_{1,2}$=7.5 Hz, H1), 5.02 (1H, dd, $J_{2,3}$=9.0 Hz, H2), 5.27 (1H, t, $J_{3,4}$=9.0 Hz, H3), 5.22 (1H, t, $J_{4,5}$=9.0 Hz, H4), 4.04 (1H, d, H5), 2.02 (6H, s, 2Ac), 2.04 (3H, s, Ac), 3.34 (3H, s, Me, ether), 3.75 (3H, s, Me, ester); ^{13}C NMR ($CDCl_3$) δ=100.9 (C1), 71.2 (C2), 72.1 (C3), 69.5 (C4), 72.6 (C5), 167.2 (C6), 59.0 (Me, ether), 52.9 (Me, ester), 20.5, 20.6 (2C) (Ac).

Fond: C, 48.52; H, 6.31%. Calcd for $C_{16}H_{24}O_{11}$: C, 48.98; H, 6.17%.

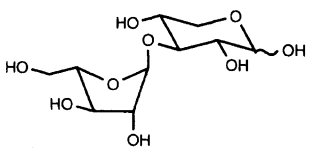
Methyl (2′-Methoxyethyl β-D-Glucopyranosid)uronate (11). The acetate **10** (200.0 mg, 0.51 mmol) was treated with methanolic sodium methoxide (0.15%, 5.1 ml) for 1 h at room temp. After neutralization with acetic acid and evaporation, chromatography with CM system furnished **11** (114.0 mg, 84%), mp 100—101 °C; $[\alpha]_D$ −43° (*c* 1.8, H_2O); ^{1}H NMR (D_2O) δ=4.54 (1H, d, $J_{1,2}$=7.5 Hz, H1), 3.35 (1H, dd, $J_{2,3}$=9.0 Hz, H2), 3.53 (1H, t, $J_{3,4}$=9.0 Hz, H3), 3.59 (1H, t, $J_{4,5}$=9.0 Hz, H4), 4.07 (1H, d, H5), 3.83 (3H, s, Me, ester), 3.38 (3H, s, Me, ether); ^{13}C NMR (D_2O) δ=105.8 (C1), 76.1 (C2), 78.4 (C3), 74.6 (C4), 77.9 (C5), 174.2 (C6), 61.4 (Me, ester), 56.4 (Me, ether).

Found: C, 43.47; H, 7.01%. Calcd for $C_{10}H_{18}O_8 \cdot 0.5H_2O$: C, 43.63; H, 6.96%.

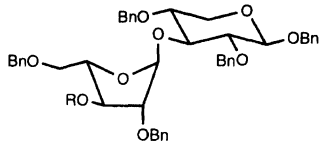
Benzyl (2′-Methoxyethyl 2,3,4-Tri-*O*-benzyl-β-D-glucopyranosid)uronate (12). Compound **11** (188.5 mg, 0.71 mmol) was treated with aq NaOH (2%, 1.25 ml, 0.63 mmol) for 3h at 25 °C. After freeze-drying, the residue was stirred in dimethyl sulfoxide (2.0 ml) containing benzyl bromide (0.43 ml) and NaH (ca. 40% dispersion in oil, 293.5 mg) at 15 °C for 15 min. After storage at 0 °C for 30 min, the mixture was processed in the manner described for the preparation of **8** and chromatographed with HE system to give **12** (141.8 mg, 33%), mp 93—94 °C; $[\alpha]_D$ −17° (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.52 (1H, d, $J_{1,2}$=7.5 Hz, H1), 3.54 (1H, dd, $J_{2,3}$=9.0 Hz, H2), 3.67 (1H, t, $J_{3,4}$=9.0 Hz, H3), 3.85 (1H, quasi t, $J_{4,5}$=9.5 Hz, H4), 3.95 (1H, d, H5), 3.38 (3H, s, Me); ^{13}C NMR



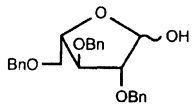
58 R = AL (β-Anomer **59**)
63 R = Bn (β-Anomer **64**)
70 R = Ns



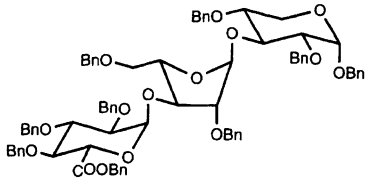
67



60 R = AL (β-Anomer **61**)
65 R = Bn (β-Anomer **66**)



62



68 (β-Anomer **69**)

Chart 7.

($CDCl_3$) δ=104.1 (C1), 81.6 (C2), 83.7 (C3), 79.2 (C4), 74.6 (C5), 168.4 (C6), 58.9 (Me), 67.2 (benzyl, ester).

Found: C, 72.08; H, 6.61%. Calcd for $C_{37}H_{40}O_8$: C, 72.53; H, 6.58%.

Methyl 2,3,4-Tri-*O*-benzyl-D-glucopyranuronate (2). Compound **8** (1.940 g, 3.7 mmol) was refluxed in a mixture of ethanol, benzene, and H_2O (7 : 3 : 1, 184 ml) in the presence of tris (triphenylphosphine)rhodium(I) chloride (0.60 g) overnight.[11] After removal of the solvents, the residue was heated in acetone (113 ml) containing dil HCl (3.5%, 3.4 ml) at 45 °C for 6 h. Evaporation and chromatography with TK system gave **2** (1.049 g, 59%), mp 110—112 °C; $[\alpha]_D$ +6° (*c* 0.8, $CHCl_3$) (lit,[6] mp 110—112 °C; $[\alpha]_D$ +25.8° (*c* 1, $CHCl_3$)); ^{1}H NMR ## ($CDCl_3$) (80%α) δ=3.24 (OH1), 5.22 (d, $J_{1,2}$=3.5 Hz, H1α), 4.75 (d, $J_{1,2}$=7.5 Hz, H1β), 3.61 (dd, $J_{2,3}$=9.0 Hz, H2α), 3.45 (dd, $J_{2,3}$=9.0 Hz, H2β), 3.98 (t, $J_{3,4}$=9.0 Hz, H3α), 3.68 (t, $J_{3,4}$=9.0 Hz, H3β), 3.76 (t, $J_{4,5}$=9.0 Hz, H4α), 3.85 (t, $J_{4,5}$=9.0 Hz, H4β), 4.49 (d, H5α), 3.99 (d, H5β), 3.70 (s, Meα), 3.72 (s, Meβ); ^{13}C NMR ($CDCl_3$) δ=91.6 (C1α), 97.7 (C1β), 79.1[8] (C2α), 82.5 (C2β), 80.7 (C3α), 83.6 (C3β), 79.2[1] (C4α), 79.1 (C4β), 70.4 (C5α), 74.4 (C5β), 170.1 (C6α), 169.3 (C6β).

Found: C, 70.21; H, 6.42%. Calcd for $C_{28}H_{30}O_7$; C, 70.28; H, 6.32%.

Benzyl 2,3,4-Tri-*O*-benzyl-D-glucopyranuronate (3). A mixture of **9** (1.517 g, 2.55 mmol), $PdCl_2$ (200 mg), sodium acetate (200 mg) and aq acetic acid (90%, 10 ml) was stirred for 1.5 h at 60 °C.[13] Filtration, evaporation, and chromatography with TK system afforded **9** (1.180 g, 83%), mp 124—125 °C; $[\alpha]_D$ −10° (*c* 0.5, $CHCl_3$) (lit,[7] mp 124—125 °C; 130—132 °C, $[\alpha]_D$ −12° (*c* 1, $CHCl_3$); $[\alpha]_D$ +7.2° (*c* 1, $CHCl_3$)); ^{1}H NMR ($CDCl_3$) (80%α) δ=3.36 (OH1), 5.24 (d, $J_{1,2}$=3.5 Hz, H1α), 4.74 (d, $J_{1,2}$=7.5 Hz, H1β), 3.62 (dd, $J_{2,3}$=9.0 Hz, H2α), 3.47 (dd, $J_{2,3}$=9.0 Hz, H2β), 4.00 (t, $J_{3,4}$=9.0 Hz, H3α), 3.68 (t, $J_{3,4}$=9.0 Hz, H3β), 3.79 (t, $J_{4,5}$=9.0 Hz, H4α), 3.87 (t, $J_{4,5}$=9.0 Hz, H4β), 4.54 (d, H5α), 4.62 (d, H5β); ^{13}C NMR ($CDCl_3$) δ=91.6 (C1α), 97.7 (C1β), 79.1[6] (C2α), 82.5 (C2β), 80.6 (C3α), 83.6 (C3β), 79.7 (C4α), 79.2[2] (C4β), 70.6 (C5α), 74.6 (C5β), 169.6 (C6α), 168.7 (C6β).

Found: C, 73.75; H, 6.27%. Calcd for $C_{34}H_{34}O_7$: C, 73.63; H, 6.18%).

Treatment of the 2-Methoxyethyl Compound 12. To a stirred solution of **12** (50.0 mg, 0.082 mmol) in dichloromethane (1.0 ml) was added $TiCl_4$ (8.7 μl).[14] Processing and chromatography with TK system gave **benzyl (2′-methoxyethyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosid)uronate (13);** (24.3 g, 49%); $[\alpha]_D$ +23° (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.86 (1H, d, $J_{1,2}$=3.5 Hz, H1), 3.59 (1H, dd, $J_{2,3}$=9.0 Hz, H2), 4.01 (1H, t, $J_{3,4}$=9.0 Hz, H3), 3.73 (1H, quasi t, $J_{4,5}$=9.5 Hz H4), 4.36 (1H, d, H5), 3.34 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ=97.8 (C1), 79.4 (C2), 81.3 (C3), 79.7 (C4), 70.5 (C5), 167.9 (C6), 58.9 (Me) (Found: C; 72.26; H, 6.51%. Calcd for $C_{37}H_{40}O_8$: C, 72.53; H, 6.58%).

After elution of **13**, the donor **3** (9.4 mg, 21%) was obtained.

Benzyl *O*-(Methyl 2,3,4-Tri-*O*-benzyl-α- and -β-D-glucopyranosyluronate)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosides (18 and 19). Triethylamine (64.5 μl) was added into a stirred mixture of donor **2** (115.0 mg, 0.241 mmol), acceptor **14** (100.0 mg, 0.185 mmol), *p*-nitrobenzenesulfonyl chloride (102.5 mg), silver trifluoromethanesulfonate (118.8 mg), and dichloromethane (1.0 ml) at −50 °C. The bath temp was allowed to rise to 0 °C. After being stirred overnight, the reaction mixture was processed in the manner described previously.[3,29] Chromatogra-

For the equilibrated anomeric mixtures of the reducing sugars (**2**, **3**, **46**, and the compounds in Tables 2, 3, and 4), each atom in both anomers is numbered as 1α and 1β, 2α and 2β, and so on.

Table 4. ^{13}C NMR Spectral Data of α-D-GlcA*p*-(1→3)-α-L-Ar a*f*-(1→3)-D-Xyl

A component of plantago-mucilage A from the seeds of *Plantago asatica* Linné constituing a Chinese medincine chegianzi [車前子], and the related pentobioside, α-L-Ara*f*-(1→3)-D-Xyl (75.5 MHz, in D_2O)[a)]

C	44		67	
	α	β	α	β
1	95.6	99.9	95.6	99.9
2	74.6	77.4	74.6	77.4
3	82.8	85.5	82.8	85.4
4	71.3	71.2	71.3[4]	71.2[6]
5	64.5	68.5	64.4	68.4
1′	111.9	111.9	111.5[9]	111.5[5]
2′	82.4	82.4	84.6	84.6
3′	87.8	87.7	79.8	79.8
4′	86.5	86.6	87.2[7]	87.3[4]
5′	64.8	64.8	64.6	64.6
1″	102.4[1]	102.3[6]		
2″	74.3	74.3		
3″	76.0	76.0		
4″	74.9	74.9		
5″	74.9	74.9		
6″	177.6	177.6		

a) The carbons in the reducing D-Xyl moiety are numbered without prime and those in the α-L-Ara*f* moiety are did with prime, whereas those in the α-D-GlcA*p* moiety are coded with the doubly primed number.

phy using TK system gave **18** (98.6 mg, 53%); $[\alpha]_D$ +25° (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.67 (1H, d, $J_{1,2}$=7.5 Hz, H1), 5.81 (1H, d, $J_{1',2'}$=3.5 Hz, H1′), 3.91 (1H, dd, $J_{2,3}$=9.0 Hz, H2), 4.68 (d, $J_{4',5'}$=9.5 Hz, H5′), 3.54 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ=102.8 (C1), 95.3 (C1′), 75.4 (C2), 78.4 (C2′), 83.1 (C3), 80.7 (C3′), 78.7 (C4), 80.1 (C4′), 75.2 (C5), 70.1 (C5′), 68.7 (C6), 170.4 (C6′), 52.1 (Me),

and **19** (53.3 mg, 29%); $[\alpha]_D$ +3° (*c* 1.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.57 (1H, d, $J_{1,2}$=7.5 Hz, H1), 4.96 (1H, d, $J_{1',2'}$=7.5 Hz, H1′), 3.94 (1H, dd, $J_{2,3}$=9.0 Hz, H2), 3.79 (1H, d, $J_{4',5'}$=9.5 Hz, H5′), 3.66 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ=100.9 (C1), 102.5 (C1′), 78.6 (C2), 82.5 (C2′), 85.3 (C3), 84.0 (C3′), 78.1 (C4), 79.3 (C4′), 75.0 (C5), 74.2 (C5′), 68.9 (C6), 168.8 (C6′), 52.3 (Me).

Found: **18**: C, 73.90; H, 6.47% and **19**: C, 73.81; H, 6.50%. Calcd for $C_{62}H_{64}O_{12}$: C, 74.38; H, 6.44%.

Similarly, **2** was condensed with **15**, **16**, and **17** to give the anomeric pairs of **20** and **21**, **22** and **23**, and **24** and **25**, respectively (Table 1).

Benzyl *O*-(Methyl 2,3,4-Tri-*O*-benzyl-α- and -β-D-glucopyranosyluronate)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranosides (20 and 21). Chromatography with DE system gave **20** (51%), $[\alpha]_D$ +16° (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.54 (1H, d, $J_{1,2}$=7.5 Hz, H1), 5.57 (1H, d, $J_{1',2'}$=3.5 Hz, H1), 3.95 (1H, quasi t, $J_{2,3}$=9.0 Hz, $J_{3,4}$=9.5 Hz, H3), 4.83 (1H, d, $J_{4',5'}$=9.5 Hz, H5′), 3.53 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ=102.7 (C1), 97.6 (C1′), 79.8 (C2), 79.1 (C2′), 80.3 (2C, C3 and C4), 81.3 (C3′), 78.5 (C4′), 74.6 (C5), 70.5 (C5′), 68.7 (C6), 170.7 (C6′), 52.1 (Me),

and **21** (24%), $[\alpha]_D$ +2° (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ= 4.48 (1H, d, $J_{1,2}$=7.5 Hz, H1), 5.12 (1H, d, $J_{1',2'}$=7.5 Hz, H1′), 4.05 (1H, $J_{2,3}$=$J_{3,4}$=9.0 Hz, H3), 3.77 (1H, $J_{4',5'}$=10.0 Hz, H5′), 3.62 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ=102.2 (C1), 103.0 (C1′), 83.0 (C2), 82.3 (C2′), 80.9 (C3), 84.0 (C3′), 76.1 (C4), 79.7 (C4′), 74.4 (C5), 74.3 (C5′), 68.9 (C6), 168.8 (C6′), 52.3 (Me).

Found: **20**: C, 74.12; H, 6.55% and **21**: C, 74.26; H, 6.63%. Calcd for $C_{62}H_{64}O_{12}$: C, 74.38; H, 6.44%.

Benzyl *O*-(Methyl 2,3,4-Tri-*O*-benzyl-α- and -β-D-glucopyranosyluronate)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (22 and 23). Chromatography with TK system gave **22** (64%); $[\alpha]_D$ +12° (*c* 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.55 (1H, d, $J_{1,2}$=7.5 Hz, H1), 5.73 (1H, d, $J_{1',2'}$=3.5 Hz, H1′), 4.10 (1H, quasi t, $J_{3,4}$=9.0 Hz, $J_{4,5}$=9.5 Hz, H4), 4.34 (1H, d, $J_{4',5'}$=9.5 Hz, H5′), 3.56 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ=102.2 (C1), 97.1 (C1′), 82.2 (C2), 78.6 (C2′), 84.6 (C3), 81.0 (C3′), 73.5 (C4), 79.7 (C4′), 74.2 (C5), 71.1 (C5′), 69.2 (C6), 170.1 (C6′), 52.2 (Me),

and **23** (25%), mp 101—102 °C; $[\alpha]_D$ +5° (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.48 (1H, d, $J_{1,2}$=7.5 Hz, H1), 4.58 (1H, d, $J_{1',2'}$=7.5 Hz, H1′), 4.05 (1H, quasi t, $J_{3,4}$=9.0 Hz, $J_{4,5}$=9.5 Hz, H4), 3.77 (1H, d, $J_{4',5'}$=9.0 Hz, H5′), 3.58 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ=102.5 (C1), 102.7 (C1′), 81.7 (C2), 82.2 (C2′), 82.9 (C3), 84.0 (C3′), 77.1 (C4), 79.6 (C4′), 75.0 (C5), 74.4 (C5′), 67.9 (C6), 168.8 (C6′), 52.2 (Me).

Found: **22**: C, 74.23: H, 6.55% and **23**: C, 74.03; H, 6.56%. Calcd for $C_{62}H_{64}O_{12}$: C, 74.38; H, 6.44%.

Benzyl *O*-(Methyl 2,3,4-Tri-*O*-benzyl-α- and -β-D-glucopyranosyluronate)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranosides (24 and 25). Chromatography with TK system gave **24** (44%), $[\alpha]_D$ +67° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.80 (1H, d, $J_{1,2}$=3.5 Hz, H1), 4.98 (1H, d, $J_{1',2'}$=3.5 Hz, H1′), 4.37 (1H, d, $J_{4',5'}$=9.5 Hz, H5′), 3.73 (1H, dd, $J_{5,6a}$=1.5 Hz, $J_{6a,6b}$=11.5 Hz, H6a), 3.84 (1H, dd, $J_{5,6b}$=4.5 Hz, H6b), 3.67 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ=94.8 (Cl), 97.8 (Cl′), 80.1 (C2), 79.4 (C2′), 82.1 (C3), 81.0 (C3′), 77.8 (C4), 79.6 (C4′), 70.6 (C5), 70.3 (C5′), 66.7 (C6), 170.3 (C6′), 52.3 (Me),

and **25** (42%), mp 119—120 °C; $[\alpha]_D$ +23 ° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.82 (1H, d, $J_{1,2}$=3.5 Hz, H1), 4.41 (1H, d, $J_{1',2'}$=7.5 Hz, H1′), 3.85 (1H, d, $J_{4',5'}$=9.0 Hz, H5′), 4.01 (1H, dd, $J_{5,6a}$=1.5 Hz, $J_{6a,6b}$=9.5 Hz, H6a), 4.11 (1H, dd, $J_{5,6b}$=4.0 Hz, H6b), 3.72 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ=95.1 (C1), 104.0 (C1′), 79.9 (C2), 81.6 (C2′), 81.9 (C3), 84.0 (C3′), 78.0 (C4), 79.2 (C4′), 70.2 (C5), 74.5 (C5′), 68.8 (C6), 168.8 (C6′), 52.4 (Me).

Found: **24**: C, 74.33; H, 6.56% and **25**: C, 74.09; H, 6.40%. Calcd for $C_{62}H_{64}O_{12}$: C, 74.38; H, 6.44%.

Benzyl *O*-(Benzyl 2,3,4-Tri-*O*-benzyl-α- and -β-D-glucopyranosyluronate)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosides (36 and 37). The donor **3** (72.0 mg, 0.13 mmol) was condensed with the acceptor **14** (54.0 mg, 0.10 mmol), in the manner described above for the cross-condensation of **2** and **14**, using *p*-nitrobenzenesulfonyl chroride (55.4 mg), silver trifluoromethanesulfonate (64.3 mg), triethylamine (34.9 μl), and dichloromethane (0.54 ml). Processing[3,29] and chromatography using DE system gave **36** (57.0 mg, 53%), $[\alpha]_D$ +15° (*c* 1.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.72 (1H, d, $J_{1,2}$=7.5 Hz, H1), 5.83 (1H, d, $J_{1',2'}$=3.5 Hz, H1′), 3.96 (1H, dd, $J_{2,3}$=9.0 Hz, H2), 4.80 (1H, d, $J_{4',5'}$=9.0 Hz, H5′); ^{13}C NMR ($CDCl_3$) δ=102.7 (C1), 95.2 (C1′), 75.1 (C2), 78.4 (C2′), 83.1 (C3), 80.7 (C3′), 78.6 (C4), 79.8 (C4′), 75.1 (C5), 70.4 (C5′), 68.7 (C6), 170.1 (C6′), 66.8 (benzyl, ester),

and **37** (29.3 mg, 27%), mp 96—97 °C; $[\alpha]_D$ −14° (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.56 (1H, d, $J_{1,2}$=7.5 Hz, H1), 4.99 (1H, d, $J_{1',2'}$=7.5 Hz, H1′), 3.94 (1H, dd, $J_{2,3}$=9.0 Hz, H2), 3.83 (1H, d, J=9.5 Hz, H5′); ^{13}C NMR ($CDCl_3$)δ=100.8 (C1), 102.4 (C1′), 78.6 (C2), 82.5 (C2′), 85.3 (C3), 84.0 (C3′), 78.1 (C4), 79.4

(C4′), 74.9 (C5), 74.4 (C5′), 68.9 (C6), 168.3 (C6′), 67.2 (benzyl, ester).

Found: **36**: C, 75.83; H, 6.43% and **37**: C, 75.54; H, 6.26%. Calcd for $C_{68}H_{68}O_{12}$: C, 75.81; H, 6.36%.

Similarly, **3** was condensed with **15**, **16**, and **17** to give the anomeric pairs of **38** and **39**, **40** and **41**, and, **42** and **43**.

Benzyl *O*-(Benzyl 2,3,4-Tri-*O*-benzyl-α- and -β-D-glucopyranosyluronate)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranosides (38 and 39). Chromatography with HE system gave **39** (21%), $[\alpha]_D$ −12° (*c* 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.47 (1H, d, $J_{1,2}$=7.5 Hz, H1), 5.01 (1H, d, $J_{1',2'}$=7.5 Hz, H1′), 4.06 (1H, $J_{2,3}$=$J_{3,4}$=9.0 Hz, H3), 3.80 (1H, d, $J_{4',5'}$=9.5 Hz, H5′); ^{13}C NMR ($CDCl_3$) δ=102.3 (C1), 103.0 (C1′), 83.0 (C2), 82.3 (C2′), 80.9 (C3), 84.0 (C3′), 76.1 (C4), 79.8 (C4′), 74.6 (C5), 74.4 (C5′), 69.0 (C6), 168.3 (C6′), 67.0 (benzyl, ester),

and **38** (56%), $[\alpha]_D$ +10° (*c* 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.55 (1H, d, $J_{1,2}$=7.5 Hz, H1), 5.59 (1H, d, $J_{1',2'}$=3.5 Hz, H1′), 3.98 (1H, $J_{2,3}$=$J_{3,4}$=9.0 Hz, H3), 4.91 (1H, d, $J_{4',5'}$=9.5 Hz, H5′); ^{13}C NMR ($CDCl_3$) δ=102.7 (C1), 97.7 (C1′), 79.8 (C2), 79.3 (C2′), 81.1^5 (C3), 81.2^0 (C3′), 78.2 (C4), 80.0 (C4′), 74.5 (C5), 70.9 (C5′), 68.7 (C6), 169.9 (C6′), 67.0 (benzyl, ester).

Found: **38**: C, 75.57; H, 6.48% and **39**: C, 75.67; H, 6.47%. Calcd for $C_{68}H_{68}O_{12}$: C, 75.81; H, 6.36%.

Benzyl *O*-(Benzyl 2,3,4-Tri-*O*-benzyl-α- and -β-D-glucopyranosyluronate)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (40 and 41). Chromatography with TK system gave **40** (66%), mp 93—94 °C; $[\alpha]_D$ −1° (*c* 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.53 (1H, d, $J_{1,2}$=7.5 Hz, H1), 5.69 (1H, d, $J_{1',2'}$=3.5 Hz, H1′), 4.06 (1H, t, $J_{3,4}$=$J_{4,5}$=9.0 Hz, H4), 4.38 (1H, d, $J_{4',5'}$=9.5 Hz, H5′); ^{13}C NMR ($CDCl_3$) δ=102.2 (C1), 97.4 (C1′), 82.1 (C2), 78.6 (C2′), 84.5 (C3), 81.0 (C3′), 73.8 (C4), 79.6 (C4′), 74.3 (C5), 71.4 (C5′), 69.2 (C6), 169.6 (C6′), 67.2 (benzyl, ester),

and **41** (24%), mp 118—119 °C; $[\alpha]_D$ −8° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.47 (1H, d, $J_{1,2}$=7.5 Hz, H1), 4.59 (1H, d, $J_{1',2'}$=7.5 Hz, H1′), 4.05 (1H, t, $J_{3,4}$=$J_{4,5}$=9.0 Hz, H4), 3.80 (1H, d, $J_{4',5'}$=9.5 Hz, H5′) ; ^{13}C NMR ($CDCl_3$) δ=102.5 (C1), 102.6 (C1′), 81.8 (C2), 82.2 (C2′), 82.8 (C3), 84.0 (C3′), 77.0 (C4), 79.7 (C4′), 75.0 (C5), 74.5 (C5′), 67.9 (C6), 168.2 (C6′), 67.1 (benzyl, ester).

Found: **40**: C, 75.80; H, 6.44% and **41**: C, 75.80; H, 6.47%. Calcd for $C_{68}H_{68}O_{12}$: C, 75.81; H, 6.36%.

Benzyl *O*-(Benzyl 2,3,4-Tri-*O*-benzyl-α- and -β-D-glucopyranosyluronate)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranosides (42 and 43). Chromatography with TK system gave **43** (40%), mp 136—137 °C; $[\alpha]_D$ +42° (*c* 3.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.88 (1H, d, $J_{1,2}$=3.5 Hz, H1), 4.45 (1H, d, $J_{1',2'}$=7.5 Hz, H1′), 3.94 (1H, d, $J_{4',5'}$=9.5 Hz, H5′), 3.69 (1H, dd, $J_{5,6a}$=3.0 Hz, $J_{6a,6b}$=11.0 Hz, H6a), 4.15 (1H, dd, $J_{5,6b}$=2.0 Hz, H6b); ^{13}C NMR ($CDCl_3$) δ=95.1 (C1), 104.0 (C1′), 79.9 (C2), 81.5 (C2′), 81.9 (C3) 83.9 (C3′), 77.9 (C4), 79.3 (C4′), 70.1 (C5), 74.7 (C5′), 68.7 (C6), 168.2 (C6′), 67.2 (benzyl, ester),

and **42** (43%), $[\alpha]_D$ +55° (*c* 2.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.78 (1H, d, $J_{1,2}$=3.5 Hz, H1), 5.01 (1H, d, $J_{1',2'}$=3.5 Hz, H1′), 4.46 (1H, d, $J_{4',5'}$=9.5 Hz, H5′), 3.76 (1H, dd, $J_{5,6a}$=1.0 Hz, $J_{6a,6b}$=11.0 Hz, H6a), 3.85 (1H, dd, $J_{5,6b}$=5.0 Hz, H6b); ^{13}C NMR ($CDCl_3$) δ=94.8 (C1), 97.8 (C1′), 80.1 (2C, C2 and C3′), 79.4 (C2′), 82.0 (C3), 77.8 (C4), 79.7 (C4′), 70.6 (2C, C5 and C5′), 66.7 (C6), 169.8 (C6′), 67.1 (benzyl, ester).

Found: **42**: C, 75.43; H, 6.50% and **43**: C, 75.19; H, 6.35%. Calcd for $C_{68}H_{68}O_{12}$: C, 75.81; H, 6.36%.

***O*-(Methyl α-D-Glucopyranosyluronate)-(1→2)-D-glucopyranose (26).** Hydrogenolysis of **18** (39.0 mg, 0.039 mmol) over Pd on C (10%, 15.9 mg) in acetic acid (6.0 ml) for 24 h at 25 °C under 340 kPa of H_2 using a Parr-3911 hydrogenation apparatus. After filtration, the solvent was removed at 35 °C in vacuo. The residue was chromatographed on using CM system and the trituration with acetone gave powdery **26** (12.2 mg, 85%), $[\alpha]_D$ +63° (*c* 0.5, H_2O); ^{1}H NMR (D_2O) (31%α) δ=5.04 (d, $J_{1,2}$=3.5 Hz, H1α), 4.71 (d, $J_{1,2}$=7.5 Hz, H1β), 5.32 (d, $J_{1',2'}$=3.5 Hz, H1′α), 5.30 (d, $J_{1',2'}$=3.5 Hz, H1′β), 4.52 (d, $J_{4',5'}$=10.0 Hz, H5′α), 4.61 (d, $J_{4',5'}$=10.0 Hz, H5′β), 3.74 (3H, s, Me).

Found: C, 42.40: H, 5.97%. Calcd for $C_{13}H_{22}O_{12}$: C, 42.16; H, 5.99%.

Similarly, **20**, **22**, **24**, and **25** was converted into the corresponding methyl esters **27**, **28**, **29**, and **30**.

***O*-(Methyl α-D-Glucopyranosyluronate)-(1→3)-D-glucopyranose (27).** 78%, $[\alpha]_D$ +98° (*c* 0.9, H_2O); ^{1}H NMR (D_2O) (42%α) δ=5.14 (d, $J_{1,2}$=3.5 Hz, H1α), 4.55 (d, $J_{1,2}$=7.5 Hz, H1β), 5.31 (d, $J_{1',2'}$=3.5 Hz, H1′α), 5.30 (d, $J_{1',2'}$=3.5 Hz, H1′β), 4.55 (d, $J_{4',5'}$=10.0 Hz, H5′α), 4.61 (d, $J_{4',5'}$=10.0 Hz, H5′β), 3.73 (3H, s, Me).

Found: C, 42.19; H, 6.08%. Calcd for $C_{13}H_{22}O_{12}$: C, 42.16; H, 5.99%.

***O*-(Methyl α-D-Glucopyranosyluronate)-(1→4)-D-glucopyranose (28).** 68%, $[\alpha]_D$ +94° (*c* 0.5, H_2O); ^{1}H NMR (D_2O) (40%α) δ=5.13 (d, $J_{1,2}$=3.5 Hz, H1α), 4.56 (d, $J_{1,2}$=8.0 Hz, H1β), 5.42 (1H, d, $J_{1',2'}$=3.5 Hz, H1′), 4.21 (d, $J_{4',5'}$=9.5 Hz, H5′α), 4.20 (d, $J_{4',5'}$=9.5 Hz, H5′β), 3.75 (3H, s, Me).

Found: C, 41.24; H, 6.43%. Calcd for $C_{13}H_{22}O_{12}\cdot 0.5H_2O$: C, 41.16; H, 6.11%.

***O*-(Methyl α-D-Glucopyranosyluronate)-(1→6)-D-glucopyranose (29).** 76%, $[\alpha]_D$ +80° (*c* 0.3, H_2O); ^{1}H NMR (D_2O) (35%α) δ=5.15 (d, $J_{1,2}$=3.5 Hz, H1α), 4.59 (d, $J_{1,2}$=7.5 Hz, H1β), 4.93 (d, $J_{1',2'}$=3.5 Hz, H1′α), 4.94 (d, $J_{1',2'}$=3.5 Hz, H1′β), 4.24 (d, $J_{4',5'}$=9.5 Hz, H5′α), 4.26 (d, $J_{4',5'}$=9.5 Hz, H5′β), 3.74 (3H, s, Me).

Found: C, 41.22; H, 6.08%. Calcd for $C_{13}H_{22}O_{12}\cdot 0.5H_2O$: C, 41.16; H, 6.11%.

***O*-(Methyl β-D-Glucopyranosyluronate)-(1→6)-D-glucopyranose (30).** 82%, $[\alpha]_D$ −3° (*c* 0.7, H_2O); ^{1}H NMR (D_2O) (40%α) δ=5.21 (d, $J_{1,2}$=3.5 Hz, H1α), 4.64 (d, $J_{1,2}$=7.5 Hz, H1β), 4.56 (d, $J_{1',2'}$=7.5 Hz, H1′α), 4.58 (d, $J_{1',2'}$=7.5 Hz, H1′β), 4.08 (d, $J_{4',5'}$=9.0 Hz, H5′α), 4.07 (d, $J_{4',5'}$=9.0 Hz, H5′β), 3.82 (3H, s, Me).

Found: C, 38.83; H, 6.32%. Calcd for $C_{13}H_{22}O_{12}\cdot 1.5H_2O$: C, 39.30; H, 6.34%.

***O*-(α-D-Glucopyranosyluronic Acid)-(1→2)-D-glucopyranose (31).** (A) Hydrogenation of **36** (34.8 mg, 0.032 mmol) over Pd on C (20 mg) in acetic acid (6.0 ml) under 340 kPa of H_2 at 25°C for 24 h and chromatography on Dowex 50W×8 with H_2O and trituration with acetone gave powdery **31** (10.0 mg, 88%), $[\alpha]_D$ +85° (*c* 0.7, H_2O) (lit,[30] $[\alpha]_D^{25}$ +65° (H_2O)); ^{1}H NMR (D_2O) (40%α) δ=5.21 (d, $J_{1,2}$=3.5 Hz, H1α), 4.79 (d, $J_{1,2}$=7.5 Hz, H1β), 5.41 (d, $J_{1',2'}$=3.5 Hz, H1′α), 5.39 (d, $J_{1',2'}$=3.5 Hz, H1′β), 4.45 (d, $J_{4',5'}$=10.0 Hz, H5′α), 4.56 (d, $J_{4',5'}$=10.0 Hz, H5′β).

Found: C, 38.59; H, 5.64%. Calcd for $C_{12}H_{20}O_{12}\cdot H_2O$: C, 38.51; H, 5.92%.

Similar hydrogenolyses of **38**, **40**, **42**, and **43** gave **32** (73%), **33** (92%), **34** (83%), and **35** (85%), respectively.

(B) A solution of **26** (13.3 mg, 0.036 mmol) in dil NaOH (0.2%, 1.08 ml) was stored at room temp overnight. The solution was chromatographed with H_2O on Dowex 50W×8 and lyophilyzed to give **31** (12.4 mg, 97%)

Similarly, **27**, **28**, **29**, and **30** was converted into **32** (93%), **33**

(94%), **34** (94%), and **35** (95%), respectively.

***O*-(α-D-Glucopyranosyluronic Acid)-(1→3)-D-glucopyranose (32).** $[\alpha]_D$ +98° (*c* 0.4, H_2O); ^1H NMR (D_2O) (40%α) δ=5.22 (d, $J_{1,2}$=3.5 Hz, H1α), 4.65 (d, $J_{1,2}$=7.5 Hz, H1β), 5.39 (1H, d, $J_{1',2'}$=3.5 Hz, H1′), 4.49 (d, $J_{4',5'}$=10.0 Hz, H5′α), 4.51 (d, $J_{4',5'}$=10.0 Hz, H5′β).

Found: C, 39.78; H, 5.87%. Calcd for $C_{12}H_{20}O_{12}\cdot 0.5H_2O$: C, 39.46; H, 5.79%.

***O*-(α-D-Glucopyranosyluronic Acid)-(1→4)-D-glucopyranose (33).** $[\alpha]_D$ +89° (*c* 0.3, H_2O) (lit,[31] $[\alpha]_D^{18}$ +108.1° (*c* 1.293, H_2O)), $[\alpha]_D^{21}$ +116° (*c* 2.52, H_2O); ^1H NMR (D_2O) (40%α) δ=5.19 (d, $J_{1,2}$=3.5 Hz, H1α), 4.62 (d, $J_{1,2}$=8.0 Hz, H1 β), 5.41 (1H, $J_{1',2'}$=3.5 Hz, H1′), 4.09 (d, $J_{4',5'}$=9.5 Hz, H5′α), 4.08 (d, $J_{4',5'}$=9.5 Hz, H5′β).

Found: C, 38.33; H, 5.93%. Calcd for $C_{12}H_{20}O_{12}\cdot H_2O$: C, 38.51; H, 5.92%.

***O*-(α-D-Glucopyranosyluronic Acid)-(1→6)-D-glucopyranose (34).** $[\alpha]_D$ +76° (*c* 0.2, H_2O) (lit,[30] $[\alpha]_D^{25}$ +57° (H_2O)); ^1H NMR (D_2O) (33%α) δ=5.16 (d, $J_{1,2}$=3.5 Hz, H1α), 4.59 (d, $J_{1,2}$=7.5 Hz, H1β), 4.90 (d, $J_{1',2'}$=3.5 Hz, H1′α), 4.91 (d, $J_{1',2'}$=3.5 Hz, H1′β), 4.05 (d, $J_{4',5'}$=10.0 Hz, H5′α), 4.06 (d, $J_{4',5'}$=10.0 Hz, H5′β).

Found: C, 40.59; H, 5.75%. Calcd for $C_{12}H_{20}O_{12}$: C, 40.45; H, 5.66%.

***O*-(β-D-Glucopyranosyluronic Acid)-(1→6)-D-glucopyranose (35).** $[\alpha]_D$ −2° (*c* 0.2, H_2O); ^1H NMR (D_2O) (38%α) δ=5.21 (d, $J_{1,2}$=3.5 Hz, H1α), 4.64 (d, $J_{1,2}$=7.5 Hz, H1β), 4.54 (d, $J_{1',2'}$=4.5 Hz, H1′α), 4.56 (d, $J_{1',2'}$=7.5 Hz, H1′α), 3.95 (1H, d, $J_{4',5'}$=9.0 Hz, H5′).

Found: C, 39.85; H, 5.65%. Calcd for $C_{12}H_{20}O_{12}\cdot 0.5H_2O$: C, 39.46; H, 5.79%.

Benzyl α- and β-D-Xylopyranosides (48 and 49) and Their Acetates (50 and 51). A mixture of D-xylose (15 g, 0.10 mol), benzyl alcohol (15 ml), and *p*-toluenesulfonic acid monohydrate (4.5 g) was stirred at 70 °C for 60 min.[20] Chloroform (75 ml) and triethylamine (3.3 ml) were added to the cooled mixture under stirring at room temp. The mixture was chromatographed with CM system to afford an anomeric mixture (14.5 g) of **48** and **49**. This (2.0 g) was rechromatographed with IE system to furnish **49** (0.59 g, 18%), mp 108—110 °C (lit,[32] mp 113—115 °C, 116—117 °C); $[\alpha]_D$ −54° (*c* 0.1, H_2O); ^{13}C NMR (D_2O) 98.5 (C1), 72.1 (C2), 74.0 (C3), 70.2 (C4), 62.1 (C5), 70.4 (benzyl),

and **48** (1.17 g, 35%), mp 121—124°C; $[\alpha]_D$ +127° (*c* 0.2, H_2O) (lit,[32] mp 127—128.5 °C, 128—129.5 °C, $[\alpha]_D^{25}$ +139.2° (*c* 4, H_2O), $[\alpha]_D^{20}$ +139° (*c* 3.93, H_2O)); ^{13}C NMR (D_2O) 104.8 (C1), 75.7 (C2), 78.4 (C3), 71.9 (C4), 67.8 (C5), 74.2 (benzyl).

Found: **48**: C, 59.72; H, 6.45% and **49**: C, 59.90; H, 6.79%. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71%.

The above-described mixture (1.5 g) of **48** and **49** was acetylated with acetic anhydride (15 ml) and pyridine (15 ml) and chromatography with DE system afforded **50** (1.46 g, 39%), $[\alpha]_D$ +128° (*c* 1.1 $CHCl_3$) (lit,[32] $[\alpha]_D^{25}$ +142.0° (*c* 3, $CHCl_3$)) and **51** (0.69 g, 18%), mp 84—86 °C; $[\alpha]_D$ −61° (*c* 1.5, $CHCl_3$) (lit,[32] mp 91—92.5 °C; $[\alpha]_D$ −86.7° (*c* 1, $CHCl_3$)).

The acetate **51** was conveniently prepared form D-xylose, using the through process.[14] To a cold mixture of acetyl bromide (22 ml) and acetic acid (15 ml), D-xylose (10 g, 67 mmol) was added under stirring at 0 °C. After being stirred at 20 °C for 1 h, the mixture was evaporated to dryness, the residue obtained was dissolved in cold nitromethane (30 ml). To this, benzyl alcohol (15 ml) and $Hg(CN)_2$ (22 g) were added under stirring. After stirring was continued at room temp, processing and chromatography silica gel with TE system gave **51** (11.34 g, 51%).

Found: **50**: C, 58.78; H, 6.09% and **51**: C, 58.70; H, 6.08%. Calcd for $C_{18}H_{22}O_8$: C, 59.01; H, 6.05%.

Benzyl 2,4-Di-*O*-benzyl-α-D-xylopyranoside (45). (A) A mixture of **48** (121.2 mg, 0.51 mmol), NaH (ca. 60% dispersion in oil, 52 mg), and benzyl chloride (2.4 ml) was stirred at 100 °C for 1.0 h.[18] Processing and chromatography using TK system afforded **45** (135.2 mg, 64%), mp 97—98 °C; $[\alpha]_D$ +103° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ=2.59 (1H, d, *J*=2.0 Hz, OH3), 4.80 (1H, d, $J_{1,2}$=3.5 Hz, H1) 3.35 (1H, dd, $J_{2,3}$=9.5 Hz, H2), 4.10 (1H, dt, $J_{3,4}$=9.5 Hz, H3), 3.50 (1H, m, H4), 3.57 (1H, quasi t, $J_{4,5a}$=9.0 Hz, $J_{5a,5b}$=10.5 Hz, H5a), 3.64 (1H, dd, $J_{4,5b}$=5.0 Hz, H5b); ^{13}C NMR ($CDCl_3$) δ=95.0 (C1), 79.3 (C2), 72.8 (C3), 77.6 (C4), 59.9 (C5).

Found: C, 74.13; H, 6.69%. Calcd for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71%.

A solution of **45** (20.1 mg), methanol (2 ml), and methanesulfonic acid (20 μl) was refluxed for 20 h. After addition of triethylamine (26 μl), evaporation and chromatography with TK system afforded the previously synthesized methyl 2,4-di-*O*-benzyl-α-D-xylopyranoside[18] (7.3 mg, 44%).

Acetylation of **45** with acetic anhydride and pyridine and chromatography with HE system afforded its acetate, ^1H NMR ($CDCl_3$) δ=4.82 (1H, d, $J_{1,2}$=3.5 Hz, H1), 3.42 (1H, dd, $J_{2,3}$=9.5 Hz, H1), 5.53 (1H, t, $J_{3,4}$=9.5 Hz, H3), 3.53 (1H, m, H4), 3.68 (1H, d, $J_{4,5a}$=7.0 Hz, H5a), 3.69 (1H, d, $J_{4,5b}$=9.5 Hz, H5b), 2.04 (3H, s, Ac); ^{13}C NMR ($CDCl_3$) δ=95.1 (C1), 77.2 (C2), 72.9 (C3), 75.9 (C4), 59.8 (C5), 21.1, 169.9 (Ac).

(B) A mixture of **50** (556 mg, 1.52 mmol), powdered KOH (0.77 g) and benzyl chloride (11.1 ml) was stirred at 110 °C for 1.0 h. This processed mixture was chromatographed using TK system to give **45** (494 mg, 77%).

Benzyl 2,4-Di-*O*-benzyl-β-D-xylopyranoside (52). A mixture of **51** (2.86 g, 7.8 mmol), powdered KOH (3.21 g) and benzyl chloride (57 ml) was stirred at 120 °C for 1.0 h. Chromatography with TE system gave **52** (2.42 g, 48%), mp 70—71 °C; $[\alpha]_D$ −34° (*c* 0.2, $CHCl_3$); ^1H NMR ($CDCl_3$) δ=2.56 (1H, d, *J*=2.0 Hz, OH3), 4.49 (1H, d, $J_{1,2}$=7.5 Hz, H1), 3.32 (1H, dd, $J_{2,3}$=9.5 Hz, H2), 3.69 (1H, t, $J_{3,4}$=9.5 Hz, H3), 3.54 (1H, m, H4), 3.25 (1H, dd, $J_{4,5a}$=9.0 Hz, $J_{5a,5b}$=11.0 Hz, H5a), 3.98 (1H, dd, $J_{4,5b}$=5.0 Hz, H5b); ^{13}C NMR ($CDCl_3$) δ=102.6 (C1), 81.0 (C2), 75.5 (C3), 77.1 (C4), 63.8 (C5).

Found: C, 74.39; H, 6.81%. Calcd for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71%.

Acetylation of **52** with acetic anhydride and pyridine and chromatography with HE system afforded its acetate, ^1H NMR ($CDCl_3$) δ=4.53 (1H, d, $J_{1,2}$=7.5 Hz, H1), 3.34 (1H, dd, $J_{2,3}$=9.5 Hz, H2), 5.14 (1H, t, $J_{3,4}$=9.5 Hz, H3), 3.54 (1H, m, H4), 3.29 (1H, dd, $J_{4,5a}$=10.0 Hz, $J_{5a,5b}$=11.5 Hz, H5a), 3.98 (1H, dd, $J_{4,5b}$=5.5 Hz, H5b), 1.93 (3H, s, Ac); ^{13}C NMR ($CDCl_3$) δ=103.1 (C1), 79.0 (C2), 74.7 (C3), 75.5 (C4), 63.7 (C5), 21.0 170.0 (Ac).

Methyl α-L-Arabinofuranoside (53). The procedure for methanolysis[33] was modified. A mixture of L-arabinose (10 g, 0.067 mol), methanol (250 ml), and methanesulfonic acid (3.8 ml) was refluxed for 1.0 h. After addition of triethylamine (11.4 ml), evaporation and chromatography with CM system afforded a homogeneous sirup (6.4 g, 59%), $[\alpha]_D$ −118° (*c* 1, H_2O) (lit,[33] $[\alpha]_D^{20}$ −128° (*c* 4.7, H_2O)); ^{13}C NMR (D_2O)[15] δ=110.9 (C1), 83.3 (C2), 79.0 (C3), 86.5 (C4), 63.8 (C5), 57.5 (Me).

Found: C, 43.73; H, 7.40%. Calcd for $C_6H_{12}O_5$: C, 43.90; H, 7.37%.

Methyl 2,5- and 3,5-Di-*O*-trityl-α-L-arabinofuranosides (54 and 55). A mixture of sirupy **53** (784.0 mg, 4.8 mmol), trityl chloride (3.06 g), and pyridine (4.0 ml) was stirred at 40 °C for 16 h. Chloroform (20 ml) and triethylamine (4.0 ml) were added to the

mixture. After removal of the volatiles under reduced pressure, the residue obtained was chromatographed with TK system to afford **54** (1.497 g, 48%), $[\alpha]_D$ −18° (*c* 7.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.17 (1H, *J*=9.0 Hz, OH3), 4.15 (1H, s, H1), 3.98 (1H, d, $J_{2,3}$=1.0 Hz, H2), 3.58 (1H, ddd, $J_{3,4}$=3.0 Hz, H3), 4.11 (1H, m, H4), 3.14 (1H, dd, $J_{4,5a}$=6.0 Hz, $J_{5a,5b}$=9.5 Hz, H5a), 3.41 (1H, dd, $J_{4,5b}$=6.5 Hz, H5b), 3.12 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ=108.0 (C1), 83.0 (C2), 78.4 (C3), 85.4 (C4), 64.6 (C5), 54.7 (Me), 86.6, 88.2 (trityl),

and **55** (0.966 g, 31%), $[\alpha]_D$ −78° (*c* 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.87 (1H, *J*=10.0 Hz, OH2), 4.89 (1H, s, H1), 3.65 (1H, d, H2), 3.86 (1H, d, $J_{3,4}$=2.5Hz, H3), 3.99 (1H, m, H4), 2.59 (1H, dd, $J_{4,5a}$=3.0 Hz, $J_{5a,5b}$=10.0 Hz, H5a), 3.35 (1H, dd, $J_{4,5b}$=2.5 Hz, H5b), 3.45 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ=109.9 C1), 79.9 (C2), 80.7 (C3), 84.7 (C4), 63.6 (C5), 54.7 (Me), 87.6 87.7 (trityl).

Found: **54**: C, 80.05; H, 6.44%. Calcd for $C_{44}H_{40}O_5 \cdot 0.5H_20$: C, 80.34; H, 6.28%.

Found: **55**; C, 79.54; H, 6.83%. Calcd for $C_{44}H_{40}O_5 \cdot H_2O$; C, 79.25; H, 6.35%.

Acetylation of **54** with acetic anhydride and pyridine and chromatography with TK system afforded the acetate, ^{1}H NMR ($CDCl_3$) δ=3.84 (1H, s, H1), 4.11 (1H, d, $J_{2,3}$=1.0 Hz), 5.21 (1H, dd, $J_{3,4}$=4.5 Hz, H3), 3.96 (1H, m, H4), 3.35 (1H, dd, $J_{4,5a}$=4.5 Hz, $J_{5a,5b}$=9.5 Hz, H5a), 3.42 (1H, dd, $J_{4,5b}$=6.0 Hz, H5b), 1.97 (3H, s, Me), 3.00 (3H, s, Ac); ^{13}C NMR ($CDCl_3$) δ=107.7 (C1), 83.2 (C2), 79.4 (C3), 81.7 (C4), 64.2 (C5), 20.9, 169.5 (Ac), 54.7 (Me), 86.8, 88.5, 143.7, 144.0 (trityl).

The minor isomer **55** was similarly converted into the corresponding acetate, ^{1}H NMR ($CDCl_3$) δ=4.71 (1H, s, H1), 4.19 (1H, s, H2), 4.04 (1, d, $J_{3,4}$=5.0 Hz, H3), 4.54 (1H, m, H4), 3.02 (1H, dd, $J_{4,5a}$=6.0 Hz, $J_{5a,5b}$=10.0 Hz, H5a), 3.33 (1H, dd, $J_{4,5b}$=2.5 Hz, H5b), 1.76 (3H, s, Ac), 3.45 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ=106.8 (C1), 82.0 (C2), 78.0 (C3), 83.6 (C4), 63.8 (C5), 20.7, 169.4 (Ac), 54.5 (Me), 143.9[5], 144.0[3] (trityl).

Methyl 3-*O*-Allyl-α-L-arabinofuranoside (56). A mixture of **54** (800.0 mg, 1.23 mmol), NaH (ca. 60% dispersion in oil, 188 mg), and allyl bromide (4.5 ml) was refluxed for 2.5 h. After filtration, the filtrate was concentrated and chromatographed with TK system. The obtained product was dissolved in chloroform (9.0 ml). To the solution methanol (1.7 ml) and trifluoroacetic acid (0.85 ml) were added under stirring at room temp. After the mixture was kept standing for 15 min, the volatiles were evaporated and the residue was chromatographed on silica gel with CM system to furnish **56** (169.6 mg, 67%), $[\alpha]_D$ −99° (*c* 0.6, $CHCl_3$); ^{1}H NMR (D_2O) δ=4.95 (1H, br, H1), 4.18 (1H, $J_{1,2}$=1.0 Hz, $J_{2,3}$=2.0 Hz, H2), 3.80 (1H, dd, $J_{3,4}$=4.5 Hz, H3), 4.10 (1H, m, H4), 3.71 (1H, $J_{4,5a}$=6.0 Hz, $J_{5a,5b}$=12.0 Hz, H5a), 3.81 (1H, dd, $J_{4,5b}$=3.5 Hz, H5b), 5.94 (1H, m, allyl), 3.39 (3H, s, Me); ^{13}C NMR (D_2O) δ=111.3 (C1), 81.0 (C2), 87.1 (C3), 85.9 (C4), 64.1 (C5), 73.9, 121.5, 136.1 (allyl), 57.2 (Me).

Found: C, 52.09; H, 7.99%. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90%.

Treatment of **56** with acetic anhydride and pyridine and chromatography with TK system gave the corresponding diacetate, ^{1}H NMR ($CDCl_3$) δ=4.90 (1H, br, H1), 5.05 (1H, d, $J_{2,3}$=1.5 Hz, H2), 3.72 (1H, ddd, $J_{3,4}$=5.0 Hz, $J_{1,3}$=1.0 Hz, H3), 2.09, 2.10 (3H, each, s, Ac) 3.40 (13H, s, Me), 5.86 (1H, m, allyl); ^{13}C NMR ($CDCl_3$) δ=107.2 (C1), 81.1 (C2), 83.5 (C3), 80.5 (C4), 63.8 (C5), 20.8, 20.9, 169.7, 170.7 (Ac), 55.0 (Me), 71.4, 118.0, 133.9 (allyl).

Methyl 3-*O*-Allyl-2,5-di-*O*-benzyl-α-L-arabinofuranoside (57). A mixture of **56** (0.960 g, 4.7 mmol), crushed KOH (1.51 g), and benzyl chloride (10 ml) was stirred at 120 °C for 1.5 h. To a cooled mixture were added toluene and H_2O under stirring. The organic layer was washed with H_2O, concentrated, and chromatographed with HE system to furnish **57** (1.23 g, 68%), $[\alpha]_D$ −38° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.97 (1H, s, H1), 3.97 (1H, dd, $J_{2,3}$=2.5 Hz, $J_{2,4}$=1.0 Hz, H2), 3.88 (1H, dd, $J_{3,4}$=6.0 Hz, H3), 4.18 (1H, m, H4), 3.65 (1H, dd, $J_{4,5a}$=5.0 Hz, $J_{5a,5b}$=10.5 Hz, H5a), 3.71 (1H, dd, $J_{4,5b}$=4.0 Hz, H5b), 5.85 (1H, m,allyl), 3.40 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ=107.2 (C1), 88.1 (C2), 83.5 (C3), 80.9 (C4), 69.9 (C5), 117.3, 134.3 (allyl), 54.9 (Me).

Found: C, 71.90; H, 6.72%. Calcd for $C_{23}H_{28}O_5$: C, 71.85; H, 7.35%.

3-*O*-Allyl-2,5-di-*O*-benzyl-α-L-arabinofuranose (46). A mixture of **57** (1.130 mg, 2.94 mmol), acetic acid (30 ml), and dil H_2SO_4 (30%, 0.50 ml) was stirred at 75 °C for 1.5 h. A cooled mixture was diluted with toluene and H_2O. The organic layer was washed with aq $NaHCO_3$ (5%) and H_2O and chromatography with HE system furnished **46** (0.864 g, 79%), $[\alpha]_D$ −12° (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) (60%α) δ=3.19 (d, *J*=8.0 Hz, OHα), 3.88 (d, *J*=10.0 Hz, OHβ), 5.39 (d, $J_{1,2}\approx$0 Hz, H1α), 5.32 (dd, $J_{1,2}$=4.5 Hz, H1β), 5.85 (1H, m, allyl); ^{13}C NMR ($CDCl_3$) δ=101.0 (C1α), 96.2 (C1β), 86.2 (C2α), 84.0 (C2β), 82.7 (C3α), 81.8 (C3β), 82.1 (C4α), 80.5 (C4β), 70.2 (C5α), 70.5(C5β).

Found: C, 68.32; H, 6.87%. Calcd for $C_{22}H_{26}O_5 \cdot H_2O$: C, 68.02; H, 7.27%.

Benzyl *O*-(3-*O*-Allyl-2,5-Di-*O*-benzyl-α- and -β-L-arabinofuranosyl)-(1→3)-2,4-di-*O*-benzyl-α-D-xylopyranosides (58 and 59). Trimethylsilyl bromide (104.7 μl) was added to a mixture of **45** (297.9 mg, 0.81 mmol), **46** (338.2 mg, 0.81 mmol), $CoBr_2$ (176.3 mg), tetrabutylammonium bromide (259.2 mg), molecular sieves 3A (876 mg) and dichloromethane (3.0 ml) under stirring at room temp. The resulting mixture was agitated overnight. Powdery $NaHCO_3$ was added to the mixture, which was stirred for 10 min. The mixture was transferred onto the top of a column of silica gel. Development of the column with DE system gave **58** (324.3 mg, 52%), $[\alpha]_D$ +38° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.77 (1H, $J_{1,2}$=3.5 Hz, H1), 5.62 (1H, s, H1), 4.25 (1H, quasi t, $J_{2,3}$=9.5 Hz, $J_{3,4}$=9.0 Hz, H3), 5.85 (1H, m, allyl); ^{13}C NMR ($CDCl_3$) δ=95.0 (C1), 106.5 (C1′), 80.3 (C2), 88.2 (C2′), 76.3 (C3), 84.1 (C3′), 76.4 (C4), 81.3 (C4′), 60.4 (C5), 69.7 (C5′), 117.0, 134.5 (allyl),

and **59** (44.5 mg, 7%), mp 64—65 °C; $[\alpha]_D$ +97° (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.76 (1H, $J_{1,2}$=3.5 Hz, H1), 5.68 (1H, d, $J_{1',2'}$=4.0 Hz, H1′), 4.29 (1H, dd, $J_{2,3}$=9.5 Hz, $J_{3,4}$=8.0 Hz, H3), 5.88 (1H, m, allyl); ^{13}C NMR ($CDCl_3$) δ=95.6 (C1), 100.8 (C1′), 78.4 (C2), 83.7 (C2′), 76.2 (C3), 83.3 (C3′), 78.9 (C4), 80.1 (C4′), 59.6 (C5), 72.3 (C5′), 116.8, 134.7 (allyl).

Found: **58**: C, 74.46; H, 6.84% and **59**: C, 74.23; H, 6.76%. Calcd for $C_{48}H_{52}O_9$: C, 74.59; H, 6.78%.

Benzyl *O*-(3-*O*-Allyl-2,5-Di-*O*-benzyl-α- and -β-L-arabinofuranosyl)-(1→3)-2,4-di-*O*-benzyl-β-D-xylopyranosides (60 and 61). Similarly, the condensation of **46** (74.0 mg, 0.20 mmol) with **52** (84.0 mg, 0.20 mmol) in the presence of trimethylsilyl bromide (26.0 μl), $CoBr_2$ (43.8 mg), tetrabutylammonium bromide (64.4 mg), and molecular sieves 3A (218 mg) in dichloromethane (0.75 ml) and chromatography using DE system afforded **60** (63.3 mg, 41%),$[\alpha]_D$ +13° (*c* 2.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.45 (1H, d, $J_{1,2}$=7.5 Hz, H1), 5.39 (1H, s, H1′), 3.88 (1H, t, $J_{2,3}$=$J_{3,4}$=9.0 Hz, H3), 5.83 (1H, m, allyl); ^{13}C NMR ($CDCl_3$) δ=103.1 (C1), 106.4 (C1′), 82.1 (C2), 88.3 (C2′), 78.1 (C3), 84.0 (C3′), 76.2 (C4), 81.2 (C4′), 64.2 (C5), 69.7 (C5′), 117.1, 134.5 (allyl),

and **61** (11.1 mg, 7%), $[\alpha]_D$ +18° (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.49 (1H, d, $J_{1,2}$=8.0 Hz, H1), 5.61 (1H, d, $J_{1',2'}$=3.5 Hz, H1′), 3.90 (1H, t, $J_{2,3}$=$J_{3,4}$=9.0 Hz, H3), 5.88 (1H, m, allyl);

^{13}C NMR $CDCl_3$) δ=103.0 (C1), 100.6 (C′), 80.2 (C2), 83.7 (C2′), 78.9 (C3), 83.0 (C3′), 78.2 (C4), 80.0 (C4′), 63.2 (C5), 72.7 (C5′), 116.8, 134.7 (allyl).

Found: **60**: C, 74.34; H, 6.89% and **61**: C, 74.57; H, 6.79%. Calcd for $C_{48}H_{52}O_9$: C, 74.59; H, 6.78%.

Benzyl *O*-(2,3,5-Tri-*O*-benzyl-α- and -β-L-arabinofuranosyl)-(1→3)-2,4-di-*O*-benzyl-α-D-xylopyranosides (63 and 64). An analogous coupling reaction of 2,3,5-tri-*O*-benzyl-L-arabinofuranose (**62**) (84.0 mg, 0.20 mmol) with **45** (84.0 mg, 0.20 mmol) and chromatography with HE system furnished **63** (69.9 mg, 43%), $[\alpha]_D$ +59° (*c* 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.76 (1H, d, $J_{1,2}$=3.5 Hz, H1), 5.63 (1H, s, H1′), 4.25 (1H, quasi t, $J_{2,3}$=9.5 Hz, $J_{3,4}$=9.0 Hz, H3); ^{13}C NMR ($CDCl_3$) δ=95.1 (C1), 106.6 (C1′), 80.3(C2), 88.2 (C2′), 76.3 (C3), 84.1 (C3′), 76.4 (C4), 82.3 (C4′), 60.4 (C5), 69.8 (C5′),

and **64** (10.5 mg, 6%), $[\alpha]_D$ +79° (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.74 (1H, d, $J_{1,2}$=3.5 Hz, H1), 5.68 (1H, d, $J_{1',2'}$=4.0 Hz, H1′), 4.27 (1H, dd, $J_{2,3}$=9.5 Hz, $J_{3,4}$=7.5 Hz, H3); ^{13}H NMR ($CDCl_3$) δ=95.6 (C1), 100.9 (C1′), 78.4 (C2), 83.8 (C2′), 76.3 (C3), 83.3 (C3′), 78.9 (C4), 80.2 (C4′), 59.6 (C5), 72.7 (C5′).

Found: **63**: C, 75.61; H, 6.65% and **64**: C, 75.63; H, 6.70%. Calcd for $C_{52}H_{54}O_9$: C, 75.89; H, 6.61%.

Benzyl *O*-(2,3,5-Tri-*O*-benzyl-α- and β-L-arabinofuranosyl)-(1→3)-2,4-di-*O*-benzyl-β-D-xylopyranosides (65 and 66). A similar condensation of **62** with **52** and chromatography using HE system gave **65** (43%), $[\alpha]_D$ −11° (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.46 (1H, d, $J_{1,2}$=7.5 Hz, H1), 5.60 (1H, s, H1′), 3.90 (1H, quasi t, $J_{2,3}$=9.0 Hz, $J_{3,4}$=9.5 Hz, H3); ^{13}H NMR ($CDCl_3$) δ=103.0 (C1), 106.4 (C1′), 82.1 (C2), 88.2 (C2′), 78.1 (C3), 83.9 (C3′), 76.2 (C4), 81.2 (C4′), 64.1 (C5), 69.7 (C5′),

and **66** (6%), $[\alpha]_D$ +9° (*c* 1.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.49 (1H, d, $J_{1,2}$=7.5 Hz, H1), 5.62 (1H, d, $J_{1',2'}$=4.0 Hz, H1′), 3.89 (1H, t, $J_{2,3}$=$J_{3,4}$=9.0 Hz, H3); ^{13}C NMR ($CDCl_3$) δ=103.1 (C1), 100.6 (C1′), 80.2 (C2), 87.8 (C2′), 78.9 (C3), 83.1 (C3′), 78.2 (C4), 80.0 (C4′), 63.2 (C5), 72.6 (C5′).

Found: **65**: C, 75.34; H, 6.72% and **66**: C, 75.63; H, 6.68%. Calcd for $C_{52}H_{54}O_9$: C, 75.89; H, 6.61%.

***O*-(α-L-Arabinofuranosyl)-(1→3)-D-xylopyranose (67).** Hydroganation of **60** (30.0 mg, 0.036 mmol) over Pd on C (10%, 20 mg) in acetic acid (6.0 ml) at room temp overnight under 340 kPa of H_2 followed by chromatography using CM system afforded **67** (8.1 mg, 79%), $[\alpha]_D$ −57° (*c* 0.5, H_2O) (lit,[34] $[\alpha]_D^{22}$ −64° (H_2O), $[\alpha]_D^{22}$ −77° (*c* 1.3, H_2O)); ^{1}H NMR (D_2O)) (40%α) δ=5.18 (d, $J_{1,2}$=3.5 Hz, H1α), 4.60 (d, $J_{1,2}$=7.5 Hz, H1β), 5.29 (d, $J_{1',2'}$=1.5 Hz, H1′α), 5.32 (d, $J_{1',2'}$=1.5 Hz, H1′β).

Found: C, 39.71; H, 6.68%. Calcd for $C_{10}H_{18}O_9 \cdot H_2O$: C, 40.00; H, 6.71%.

Benzyl *O*-(2,5-Di-*O*-benzyl-α-L-arabinofuranosyl)-(1→3)-2,4-di-*O*-benzyl-α-D-xylopyranoside (47). A mixture of **58** (153.4 mg, 0.20 mmol), $PdCl_2$ (54.0 mg), sodium acetate (54.0 mg), and aq acetic acid (90%, 3.0 ml) was agitated at 60 °C for 30 min. The cooled mixture was filtered. The filtrate was concentrated and chromatographed using TK system to give **47** (101.1 mg, 70%), $[\alpha]_D$ +28° (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.81 (1H, d, *J*=9.5 Hz, OH3′), 4.77 (1H, d, $J_{1,2}$=3.5 Hz, H1), 5.65 (1H, s, H1′), 4.25 (1H, t, $J_{2,3}$=$J_{3,4}$=9.5 Hz, H3), 4.03 (1H, ddd, $J_{2',3'}$=1.5 Hz, $J_{3',4'}$=3.0 Hz, H3′); ^{13}C NMR ($CDCl_3$) δ=94.9 (C1), 106.1 (C1′), 80.2 (C2), 87.6 (C2′), 74.6 (C3), 77.2 (C3′), 76.5 (C4), 84.4 (C4′), 60.0 (C5), 70.5 (C5′).

Found: C, 74.07; H, 6.80%. Calcd for $C_{45}H_{48}O_9$: C, 73.75; H, 6.60%.

Benzyl *O*-(Benzyl 2,3,4-Tri-*O*-benzyl-α- and -β-D-glucopyranosyluronate)-(1→3)-*O*-(2,5-di-*O*-benzyl-α-L-arabinofuranosyl)-(1→3)-2,4-di-*O*-benzyl-α-D-xylopyranoside (68 and 69). Condensation of **3** (85.4 mg, 0.154 mmol) with **47** (86.8 mg, 0.119 mmol) was carried out in the presence of *p*-nitrobenzenesulfonyl chloride (65.7 mg), silver trifluoromethanesulfonate (76.2 mg), and triethylamine (41.4 μl) in dichloromethane (1.00 ml) in a similar manner described above for the condensation of **2** and **14**. On chromatography using TK system, the first eluate was **benzyl *O*-(2,5-di-*O*-benzyl-3-*O*-*p*-nitrobenzenesulfonyl-α-L-arabinofuranosyl)-(1→3)-2,4-di-*O*-benzyl-α-D-xylopyranoside (70)** (22.4 mg, 21%), $[\alpha]_D$ +1° (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.80 (1H, d, $J_{1,2}$=3.5 Hz, H1), 5.63 (1H, s, H1′), 4.20 (1H, t, $J_{2,3}$=$J_{3,4}$=9.5 Hz, H3), 4.83 (1H, dd, $J_{2',3'}$=1.5 Hz, $J_{4',5'}$=4.5 Hz, H3′); ^{13}C NMR ($CDCl_3$) δ=94.8 (C1), 105.7 (C1′), 80.2 (C2), 86.9 (C2′), 75.7 (C3), 84.8 (C3′), 76.3 (C4), 80.1 (C4′), 60.1 (C5), 68.4 (C5′) (Found: C, 67.71; H, 5.71; N, 1.35%. Calcd for $C_{51}H_{51}NO_{13}S$: C, 66.73; H, 5.60; N, 1.53%). Then, there appeared **68** (61.6 mg, 41%), $[\alpha]_D$ +39° (*c* 2.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.69 (1H, $J_{1,2}$=3.5 Hz, H1), 5.63 (1H, s, H1′), 5.06 (1H, $J_{1'',2''}$=3.5 Hz, H1″), 4.20 (1H, dd, $J_{2,3}$=9.5 Hz, $J_{3,4}$=8.5 Hz, H3), 4.13 (1H, dd, $J_{2',3'}$=1.5 H, $J_{3',4'}$=5.0 Hz, H3′), 4.61 (1, d, $J_{4'',5''}$=10.0 Hz, H5″); ^{13}C NMR ($CDCl_3$) δ=95.0 (C1), 106.4 (C1′), 98.7 (C1″), 80.5 (C2), 88.2 (C2′), 79.3 (C2″), 76.4 (C3), 85.5 (C3′), 81.2 (C3″), 76.4 (C4), 81.7 (C4′), 79.6 (C4″), 60.4 (C5), 68.7 (C5′), 71.1 (C5″), 169.6 (C6″), 67.2 (benzyl, ester),

and **69** (37.3 mg, 25%), $[\alpha]_D$ +19° (*c* 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.76 (1H, $J_{1,2}$=3.5 Hz, H1), 5.63 (1H, s, H1′), 4.46 (1H, $J_{1'',2''}$=7.5 Hz, H1″), 4.23 (1H, quasi t, $J_{2,3}$=9.5 Hz, $J_{3,4}$=9.0 Hz, H3), 4.31 (1H, dd, $J_{2',3'}$=2.0 Hz, $J_{3',4'}$=5.5 Hz, H3′). 3.78 (1H, d, $J_{4'',5''}$=10.0 Hz, H5″); ^{13}C NMR ($CDCl_3$) δ=94.9 (C1), 106.2 (C1′), 103.2 (C1″), 80.5 (C2), 88.9 (C2′), 81.5 (C2″), 76.1 (C3), 84.0 (C3′), 83.7 (C3″), 76.6 (C4), 81.2 (C4′), 79.2 (C4″), 60.5 (C5), 68.7 (C5′), 74.4 (C5″), 168.2 (C6″), 67.2 (benzyl, ester).

Found: **68**: C, 74.47; H, 6.42% and **69**: C, 73.75; H, 6.65%. Calcd for $C_{79}H_{80}O_{15}$: C, 74.74; H, 6.35%.

***O*-α-D-Glucopyranosyluronic acid-(1→3)-*O*-α-L-arabinofuranosyl-(1→3)-D-xylopyranose (44).** Hydrogenation of **67** (32.0 mg, 0.025 mmol) was conducted over Pd on C (25 mg) in acetic acid (6.0 ml) under 340 kPa of H_2 at 25 °C overnight. After removal of the catalyst by filtration, the filtrate was evaporated to dryness in vacuo at 35 °C. The residue was chromatographed on cellulose powder (Toyo Roshi Kaisha, Ltd., 100—200 mesh) with methanol. Evaporation and trituration with acetone gave colorless powder of **44** (8.8 mg, 76%), $[\alpha]_D$ +8° (*c* 0.4, H_2O); ^{1}H NMR (D_2O) (45%α) δ=5.32 (d, $J_{1,2}$=3.5 Hz, H1α), 4.74 (d, $J_{1,2}$=7.5 Hz, H1β), 5.45 (s, H1′α), 5.48 (s, H1′β), 5.22 (1H, $J_{1'',2''}$=10.0 Hz, H5″).

Found: C, 40.24; H, 5.95%. Calcd for $C_{16}H_{26}O_{15} \cdot H_2O$: C, 40.34; H, 5.92%.

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