Pentoside Synthesis by Dehydrative Glycosylation. Synthesis of *O*-α-L-Arabinofuranosyl-(1→3)-*O*-β-D-xylopyranosyl-(1→4)-D-xylopyranose

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O-α-L-Arabinofuranosyl-(1→3)-*O*-β-D-xylopyranosyl-(1→4)-D-xylopyranose isolated from the hydrolyzate of corncobs arabinoxylan was synthesized by way of dehydrative glycosylation.

Dehydrative glycosylation has been used in the synthesis of several trisaccharides.[1] This report deals with the synthesis of the trisaccharide, *O*-α-D-arabinofuranosyl-(1→3)-*O*-β-D-xylopyranosyl-(1→4)-D-xylopyranose (**25**), isolated from the hydrolytic products of corncobs arabinoxylan by a xylanase from *Streptomyces* sp. E-86[2], using dehydrative glycosylation.[3]

Direct benzylation of methyl β-D-xylopyranoside (**1**) in benzyl chloride in the presence of lithium hydroxide and dimethyl sulfoxide afforded the 2,4-dibenzyl ether **2** in a practical yield. Benzylation of the acetate **5** in benzyl chloride with potassium hydroxide gave mainly the 2,4-dibenzyl ether **6**. On the other hand, cyclohexylidenation of benzyl α-D-xylopyranoside (**4**) gave the 2,3-acetal **7** preferentially. This was derived into the 2,3-dibenzyl ether **9** *via* a sequence of reactions: allylation, decyclohexylidenation, benzylation and deallylation. The location of the unprotected hydroxyl group of these partially benzylated xylosides was determined by observing H-1 NMR spectra of their acetates (Table 1).

Methyl 2,4-di-*O*-benzyl-α-D-xylopyranoside (**10**)[4] was allylated and then hydrolyzed into the protected xylose **11**. The 2,4-dibenzyl ether **6** was acetylated and then treated with titanium tetrachloride, followed by hydrolysis on moist silica gel, to furnish the protected xylose **12**.[5] The corresponding benzoate **13** was also obtained similarly from **6** *via* benzoylation.

Using these donors and acceptors, a stepwise synthesis of **25** was then attempted as shown in Fig. 1. The first β-xylosylation was carried out using only the allylated donor **11** for the acceptor **9** and the NSD mixture composed of *p*-nitrobenzenesulfonyl chloride (NsCl), silver trifluoromethanesulfonate (AgOTf), and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU). The

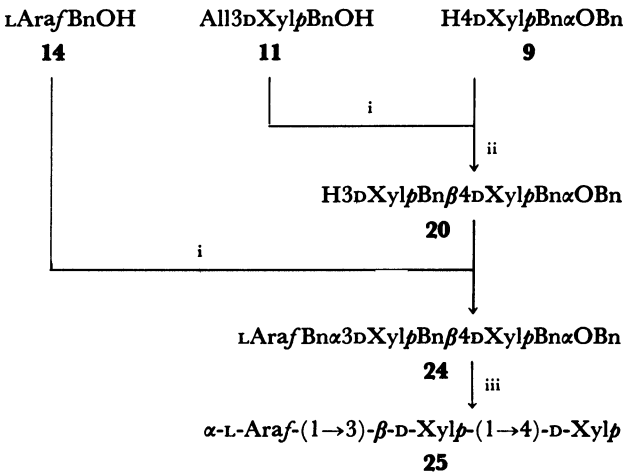
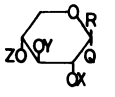


Fig. 1. Synthetic diagram of α-L-Araf-(1→3)-β-D-Xylp-(1→4)-D-Xylp.

Table 1. Data of H-1 NMR of the acetate of the partially protected D-xylopyranosides (at 90 MHz in $CDCl_3$ with TMS)

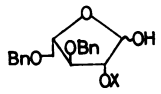
Compound	H-1	H-2	H-3	H-4	H-5e	H-5a	Me	Ac
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5e}$	$J_{4,5a}$	$J_{5e,5a}$		
2	4.29	3.27	5.13	—	3.95	—	3.51	1.91
	7.5	9.3	9.3	4.2	—	10.2		
6	4.41	3.27	5.12	—	—	—	3.34	1.93
	7.5	9.0	9.0	—	—	—		
7	5.05	3.38	3.20	4.88	3.78	4.01	—	1.97
	3.0	9.8	9.8	5.2	9.8	9.8		
8	5.11	4.81	3.99	3.49	3.93	3.79	—	2.06
	3.6	10.5	8.4	5.1	9.8	9.8		
9	4.80	3.50	3.97	4.95	3.73	3.51	—	1.93
	3.6	9.3	9.3	6.3	10.8	10.8		

reaction proceeded with a poor selectivity. Similar xylosylation using the acylated donors, **12** and **13**, gave the α-anomer selectively. The acyloxyl group at the C-3 position appears to effect for the formation of the α-anomer in this dehydrative xylosylation. The second glycosylation of the xylobiose derivarive **20** was performed using the arabinofuranosyl donor **14** and the NSD mixture. The condensation gave the desired α-anomer selectively. The acceptor **2** was also α-arabinosylated. Deprotection of the fully benzylated trisaccharide **24** gave the trisaccharide **25**, of which C-13 NMR spectrum was consistent with the proposed structure as shown in Table 3. The optical rotation value of **25** agreed well with the expected value based on the data of the relevant compounds (Table 4). Therefore, these results indicate that the trisaccharide from corncobs arabinoxylan has the structure that has been proposed.[2]



All = -$CH_2CH{=}CH_2$
Bn = -CH_2Ph
ME = -CH_2CH_2OMe

	Q	R	X	Y	Z
1	H	OMe	H	H	H
2	H	OMe	Bn	H	Bn
3	OH,	H	H	H	H
4	OBn	H	H	H	H
5	H	OME	Ac	Ac	Ac
6	H	OME	Bn	H	Bn
7	OBn	H			H
8	OBn	H	H		
9	OBn	H	Bn	Bn	H
10	OMe	H	Bn	H	Bn
11	OH,	H	Bn	All	Bn
12	OH,	H	Bn	Ac	Bn
13	OH,	H	Bn	Bz	Bn



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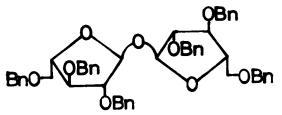

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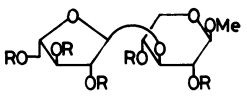
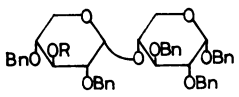
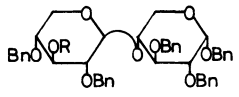


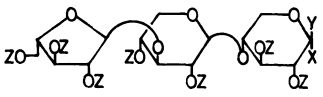
15 R=Bn
17 R=H



18 R=All
21 R=H
22 R=Ac
23 R=Bz



19 R=All
20 R=H



24 X=OBn; Y=H; Z=Bn
25 X, Y=OH, H; Z=H

Experimental

The instruments used for determining the physical characters of the compounds and chromatography have been described in previous reports.[1] The evaporation of the solvent was carried out under reduced pressure at 35—45 °C unless otherwise stated. Data regarding the chemical shifts of the anomeric carbon are in Table 2. Analytical and physical data of the compounds are summarized in Table 5.

Methyl 2,4-Di-O-benzyl-β-D-xylopyranoside (2). A mixture of methyl β-D-xylopyranoside (**1**, Pfanstiehl, 100 mg, 0.61 mmol), lithium hydroxide (88 mg)[6], dimethyl sulfoxide (0.35 ml) and benzyl chloride (2.0 ml) was vigorously stirred at 130 °C for 0.5 h. After the usual work-up, the mixture was chromatographed (gradient, toluene 2-butanone=100/1→1/1) to give the tribenzyl ether (33 mg, 2%. Found: C, 74.56; H, 6.97%), **2** (111 mg, 53%) and then a mixture of the 2,3- and the 3,4-dibenzyl ethers (78 mg, 37%. Found: C, 69,82; H, 6.95%).

Benzyl α-D-xylopyranoside (4). A mixture of D-xylose **3**, Wako, 15 g, 100 mmol), benzyl alcohol (15 ml) and *p*-toluenesulfonic acid monohydrate (4.4 g) was stirred at 75 °C for 1.5 h. After the addition of chloroform (30 ml) and triethylamine (3.6 ml), the mixture was directly chromatographed (chloroform/methanol=100/1→1/1). The obtained crude solid (6.2 g) was recrystallyzed from ethyl acetate containing 2-butanone to give pure **4** (4.5 g, 19%).

2-Methoxylethyl 2,3,4-tri-O-benzyl-β-D-xylopyranoside (5). Acetic acid (4.0 ml) was added into a stirred suspension of **3** (3.0 g, 20 mmol) in acetyl bromide (7.0 m) at 0 °C.[7]

Table 2. Chemical shifts of the anomeric carbon of the protected glycosides (at 25.1 MHz in $CDCl_3$ with TMS)

Compound	$C_{xyl}-1$ α	$C_{xyl}-1$ β	$C_{xyl}-1'$ α	$C_{xyl}-1'$ β	$C_{ara}-1''$ α
2		104.9			
9	96.1				
15		105.4			106.7
18	95.6		99.0		
19	95.8			102.8	
20	95.9			102.4	
21	95.5		98.3		
22	95.5		98.6		
23	95.5		98.5		
24	95.8			102.7	106.7

Table 3. C-13 NMR data of methyl 3-*O*-(α-L-arabinofuranosyl)-β-D-xylopyranoside and *O*-α-L-arabinofuranosyl-(1→3)-*O*-β-D-xylopyranosyl-(1→4)-D-xylopyranose (at 25.1 MHz in D_2O with ext. TMS)

C	XX[8]	MXX[9]	17	25
1α	92.8			93.4
1β	97.8	105.1		97.9
2α	72.3			72.7
2β	74.9	74.0		75.3
3α	71.9			72.3
3β	74.9	75.0		75.3
4α	77.5			77.9
4β	77.3	77.7		77.9
5α	59.8			60.2
5β	63.9	64.1		64.3
1′	102.9	103.1	105.2	103.1
2′	73.7	74.0	74.2	74.1
3′	76.5	76.9	83.3	83.0
4′	70.1	70.4	69.2	69.2
5′	66.1	66.5	66.3	66.3
1″			109.6	109.5
2″			82.6	82.6
3″			77.9	77.9
4″			85.4	85.4
5″			62.6	62.6

XX=4-*O*-(β-D-xylopyranosyl)-D-xylose, MXX=methyl 4-*O*-(β-D-xylopyranosyl)-β-D-xylopyranoside.

After being stirred at room temperature for 2 h, evaporation and co-evaporation with toluene gave a syrup. This was stirred in nitromethane (9 ml) containing 2-methoxyethanol (4.6 ml) and mercury(II) cyanide (8.6 mg). After the usual processing, the chromatography (toluene/2-butanone=100/1→1/1) of the mixture gave crude solid (5.1 g), which was crystallized with hexane containing diisopropyl ether to give **5** (1.7 g, 26%).

2-Methoxyethyl 2,4-Di-O-benzyl-β-D-xylopyranoside (6). A mixture of **5** (1.0 g, 3.0 mmol), potassium hydroxide

Table 4. Optical rotation value of *O*-α-L-arabinofuranosyl-(1→3)-*O*-β-D-xylopyranosyl-(1→4)-D-xylopyranose and related substances in water

Compound	$[\alpha]_D$(deg)	$[M]_D$(obsd)	$[M]_D$(calcd)
X	+19[10]	+29	
MX	−66[11]	−108	
MA	−135[12]	−221	
XX	−25[13]	−71	−79(X+MX)
AX	−77[2]	−217	−192(X+MA)
17	−113	−334	−329(MX+MA)
25	−17[14]	−70	−305(X+**17**)
	−88[2]	−364	−292(MA+XX)
	−72	−298	

X=D-xylose, MX=methyl β-D-xylopyranoside, MA=methyl α-L-arabinofuranoside, XX=4-*O*-(β-D-xylopyranosyl)-D-xylose, AX=3-*O*-(α-L-arabinofuranosyl)-D-xylose.

Table 5. Analytical and physical data of the compounds

Cpd.	Mp (θ_m/°C)	$[\alpha]_D^{20}$ (*c*, solv)[a]	Mol Form	Calcd(%)		Found(%)		Lit.
				C	H	C	H	
2		+2° (0.5, C)	$C_{20}H_{24}O_5$	69.75	7.02	69.71	6.89	b)
4	128—129	+140° (0.7, W)	$C_{12}H_{16}O_5$	59.99	6.71	59.55	6.67	c)
5	84—86	−49° (0.6, C)	$C_{14}H_{22}O_9$	50.30	6.63	50.26	6.61	d)
6		+8° (0.8, C)	$C_{22}H_{28}O_6$	68.02	7.27	68.16	7.21	
7		+109° (3.1, C)	$C_{18}H_{24}O_5$	67.48	7.55	67.24	7.59	
8		+118° (5.8, C)				67.18	7.59	
9	82—83	+90° (0.2, C)	$C_{26}H_{28}O_5$	74.26	6.71	74.53	6.68	e)
11	88—90	+17° (0.7, C)	$C_{22}H_{26}O_5$	71.33	7.07	70.94	6.97	
12		+19° (1.2, C)	$C_{21}H_{24}O_6$	67.73	6.50	67.22	6.42	
13	68—71	+46° (1.9, C)	$C_{26}H_{26}O_6$	71.87	6.03	71.27	5.93	
15		−7° (1.1, C)	$C_{46}H_{50}O_9$	73.97	6.75	74.27	6.66	
16		−65° (0.1, C)	$C_{52}H_{54}O_9$	75.88	6.61	75.48	6.59	
17		−113° (1.2, W)	$C_{11}H_{20}O_9 \cdot 1.5H_2O$	40.87	7.17	40.53	6.86	
18		+78° (1.4, C)	$C_{48}H_{52}O_9$	74.59	6.78	74.36	6.71	
19		+36° (1.4, C)				74.26	6.67	
20		+39° (2.2, C)	$C_{45}H_{48}O_9$	73.75	6.60	73.55	6.61	
21		+92° (2.5, C)				73.29	6.70	
22		+86° (1.8, C)	$C_{47}H_{50}O_{10}$	72.85	6.50	72.98	6.45	
23		+82° (2.5, C)	$C_{52}H_{52}O_{10}$	74.62	6.26	74.85	6.21	
24		+14° (1.5, C)	$C_{71}H_{74}O_{13}$	75.11	6.57	74.76	6.59	
25		−72° (0.5, W)	$C_{15}H_{26}O_{13} \cdot 0.5H_2O$	42.26	6.43	42.15	6.58	f)

a) C=$CHCl_3$, W=H_2O. b) Ref. 15. $[\alpha]_D^{23}$ +3° (*c* 1, $CHCl_3$). c) Ref. 16. mp 127—128.5 °C, $[\alpha]_D^{25}$ +139.2° (*c* 4, H_2O). d) Ref. 17. mp 92 °C, $[\alpha]_D^{23}$ −59.8° (*c* 2, $CHCl_3$). e) Ref. 18. $[\alpha]_D^{28}$ +15° (*c* 2, $CHCl_3$). f) Ref. 2. $[\alpha]_D^{22}$ −88° (*c* 2.5, H_2O), Ref. 14. $[\alpha]_D^{25}$ −17.3° (*c* 0.34, H_2O).

(1.5 g), and benzyl chloride (20 ml) was vigorously stirred at 120 °C for 16 h, followed by chromatography (toluene/2-butanone=100/1→1/1), to afford the tribenzyl ether (0.26 g, 18%), **6** (0.64 g, 55%), and then a mixture of the other dibenzyl ethers (0.32 g, 28%).

Benzyl 2,3- and 3,4-O-Cyclohexylidene-α-D-xylopyranosides (7 and 8). A mixture of **4** (800 mg, 3.3 mmol), 1,1-dimethoxycyclohexane (2 ml), *p*-toluenesulfonic acid monohydrate (10 mg), and *N,N*-dimethylformamide (5 ml) was heated at 120 °C for 4 h. After the addition of triethylamine (0.1 ml), the solution was evaporated at 70 °C and the obtained residue was chromatographed (toluene/2-butanone=100/1→1/1) to give **8** (117 mg, 11%) and then **7** (451 mg, 42%).

Benzyl 2,3-Di-O-benzyl-α-D-xylopyranoside (9). A mixture of **7** (0.41 g, 1.3 mmol), sodium hydride (≈60%, 0.2 g) and allyl bromide (4 ml) was stirred at 80 °C for 1 h. The mixture was filtered and the filtrate was concentrated to give a syrup which was dissolved in aq acetic acid (80%, 6 ml) containing acetone (1 ml). After kept standing for 1 h at room temperature, the solution was evaporated and co-evaporated with toluene. The obtained syrup was heated in benzyl chloride (4.5 ml) containing crushed potassium hydroxide (1.5 g) at 120 °C for 2 h. After the usual work-up, the mixture was chromatographed (toluene/2-butanone=100/1→1/1). The fully benzylated derivative thus obtained (0.54 g, 92% from **7**) was heated in dimethyl sulfoxide (2 ml) containing potassium *t*-butoxide (0.4 g) under a stream of nitrogen at 115 °C for 1 h. After dilution with toluene, the solution was washed with water and evaporated. The obtained residue was treated with acetone (10 ml) containing aq hydrochloric acid (2 M†, 0.5 ml) at room temperature for 0.5 h. After the addition of sodium hydrogencarbonate, the mixture was evaporated and chromatographed (toluene/2-butanone=100/1→1/1) to afford **9** (204 mg, 48% from **7**).

3-O-Allyl-2,4-di-O-benzyl-D-xylopyranose (11). Methyl 2,4-di-*O*-benzyl-α-D-xylopyranoside (**10**) (680 mg, 2.0 mmol) was heated in allyl bromide (7 ml) containing sodium hydride (≈60%, 168 mg) at 80 °C for 0.5 h. After filtration and evaporation, the residue was heated in aq acetic acid (80%, 5 ml) containing aq sulfuric acid (3 M, 0.8 ml) at 90 °C for 0.5 h. After the addition of sodium hydrogencarbonate (0.6 g), evaporation and chromatography (toluene/2-butanone=100/1→1/1), gave **11** (380 mg, 52%).

3-O-Acetyl-2,4-di-O-benzyl-D-xylopyranose (12). Compound **6** (245.9 mg, 0.63 mmol) was treated with acetic anhydride (2 ml) and pyridine (2 ml) overnight. The pure acetate (278.2 mg, $[\alpha]_D^{20}$ +5° (*c* 0.8, $CHCl_3$). Found: C, 67.67; H, 6.94%) obtained after a brief chromatography (toluene/2-butanone=10/1) was dissolved in dichloromethane (4.5 ml) and then treated with titanium tetrachloride (41 μl) for 15 min at room temperature. After the usual work-up, the mixture was adsorbed on a silica-gel column and chromatographed (toluene/2-butanone=100/1→1/1) to afford **12** (164.1 mg, 67%).

3-O-Benzoyl-2,4-di-O-benzyl-D-xylopyranose (13). Compound **6** (317.7 mg, 0.82 mmol) was benzoylated with benzoyl chloride (0.2 ml) and pyridine (2 ml) overnight. After the usual processing the mixture was chromatographed (toluene/2-butanone=20/1) to give pure benzoate ($[\alpha]_D^{20}$ +24° (*c* 0.8, $CHCl_3$). Found: C, 70.26, H; 6.46%). This was treated with titanium tetrachloride (57 μl) in dichloromethane (7.2 ml), followed by work-up as described for **12**, to afford **13** (234.2 mg, 73%).

Methyl 3-O-(2,3,4-Tri-O-benzyl-α-L-arabinofuranosyl)-β-D-xylopyranoside (15). DBU (45.5 μl) was added into a stirred mixture of 2,3,4-tri-*O*-benzyl-L-arabinofuranose (**14**, Pfanstiehl, 57.3 mg, 0.14 mmol), **2** (36.1 mg, 0.10 mmol), NsCl (67.5 mg), and AgOTf (78.3 mg) in dichloromethane (0.96 ml) at −55 °C. The bath temperature was rised to 0 °C at which temperature the mixture was stirred overnight. The mixture was chromatographed (toluene/2-butanone=100/1→1/1) to give the self-condensation product **16** (15.8 mg, 14%; δ_C ($CDCl_3$, TMS) 102.5 (C-1), 88.3, 84.1, 81.5, 73.6, 72.4, 72.1, 70.1) and **15** (57 mg, 73%).

Methyl 3-O-(α-L-Arabinofuranosyl)-β-D-xylopyranoside (17). The hydrogenolysis of **15** (50 mg, 0.067 mmol) over palladium on carbon (10%, 40 mg) in acetic acid (6 ml) under 340 kPa of hydrogen at room temperature overnight, followed by chromatography (chloroform/methanol=10/1=1/1), affofded **17** (15.9 mg, 80%).

Benzyl 4-O-(3-O-Allyl-2,4-di-O-benzyl-α- and -β-D-xylopyranosyl)-2,3-di-O-benzyl-α-D-xylopyranoside (18 and 19). DBU (53 μl) was added into a stirred mixture of **11** (100 mg, 0.27 mmol), **9** (87.3 mg, 0.21 mmol), NsCl (78.2 mg), and AgOTf (90.9 mg) in dichloromethane (1.0 ml) at −55 °C. The bath temperature was rised to 0 °C and then the mixture was stirred overnight. The chromatography of the reaction mixture (toluene/2-butanone=100/1→1/1) furnished **18** (27.6 mg, 17%) and then **19** (76.2 mg, 47%).

Benzyl 4-O-(2,4-Di-O-benzyl-β-D-xylopyranosyl)-2,3-di-O-benzyl-α-D-xylopyranoside (20). A mixture of **19** (93.1 mg, 0.12 mmol) and potassium *t*-butoxide (77 mg) in dimethylsulfoxide (0.4 ml) was heated at 120 °C for 6 h under a stream of nitrogen. Toluene and water were added to the solution and the organic layer was evaporated and then hydrolyzed in acetone (4 ml) containing aq hydrochloric acid (2 M, 0.1 ml) at room temperature. After addition of sodium hydrogencarbonate and concentration, chromatography (toluene/2-butanone=100/1→1/1) of the residue gave **20** (20.7 mg, 53%).

Benzyl 4-O-(2,4-Di-O-benzyl-α-D-xylopyranosyl)-2,3-di-O-benzyl-β-D-xylopyranoside (21). A mixture of **18** (27.6 mg, 0.036 mmol), tris(triphenylphosphine)rhodium(I) chloride (10 mg), ethanol (0.7 ml), benzene (0.3 ml) and water (0.1 ml) was refluxed for 5.5 h. Evaporation and treatment with aq hydrochloric acid (1 M, 0.04 ml) in acetone (1.5 ml), followed by chromatography (toluene/2-butanone=10/1), gave **21** (20.7 mg, 79%).

Benzyl 4-O-(3-O-Acetyl-2,4-di-O-benzyl-α-D-xylopyranosyl)-2,3-di-O-benzyl-α-D-xylopyranoside (22). The condensation of **12** (129.4 mg, 0.35 mmol) and **9** (112.4 mg, 0.27 mmol) was carried out using NsCl (101 mg), AgOTf (117 mg), and DBU (63.5 μl) in dichloromethane (1.42 ml) in the manner described for the synthesis of **18** and **19**. Chromatography gave **22** (45 mg, 22%). This was deacetylated in methanolic sodium methoxide (0.075 M, 2 ml) containing acetone (0.5 ml) at room temperature, followed by chromatography, to give **21**.

Benzyl 4-O-(3-O-Benzoyl-2,4-di-O-benzyl-α-D-xylopyranosyl)-2,3-di-O-benzyl-α-D-xylopyranoside (23). A similar condensation of **13** (146.6 mg, 0.34 mmol) and **9** (108.4 mg,

† 1 M=1 mol dm^{-3}.

0.26 mmol) by use of NsCl (97.3 mg), AgOTf (112.8 mg), and DBU (61.2 μl) in dichloromethane (1.39 ml) gave **23** (49.2 mg, 23%). This was treated with methanolic sodium methoxide (0.15 M, 2 ml) containing acetone (0.5 ml) at room temperature, followed by chromatography, gave **21**.

Benzyl O-(2,3,4-Tri-O-benzyl-α-L-arabinofuranosyl)-(1→3)-O-(2,4-di-O-benzyl-β-D-xylopyranosyl)-(1→4)-2,3-di-O-benzyl-α-D-xylopyranoside (24). Condensation of **14** (34.7 mg, 0.083 mmol) and **19** (46.5 mg, 0.064 mmol) was carried out using NsCl (40.9 mg), AgOTf (47.4 mg), and DBU (27.5 μl) in dichloromethane (0.58 ml) in the same manner as described above. Chromatography (toluene/2-butanone=100/1→1/1) gave **24** (54.8 mg, 76%).

O-α-L-Arabinofuranosyl-(1→3)-O-β-D-xylopyranosyl-(1→4)-D-xylopyranose (25). Hydrogenolysis of **24** (30 mg, 0.026 mmol) over palladium on carbon (10%, 30 mg) in acetic acid (6 ml) under 340 kPa of hydrogen at 25 °C overnight. Chromatography (chloroform/methanol=10/1→1/1) gave **25** (5.6 mg, 51%).

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