Synthesis of New Serine-Linked Oligosaccharides in Blood-Clotting Factors VII and IX and Protein Z. The Syntheses of *O*-α-D-Xylopyranosyl-(1→3)-D-glucopyranose, *O*-α-D-Xylopyranosyl-(1→3)-*O*-α-D-xylopyranosyl-(1→3)-D-glucopyranose, and Their Conjugates with Serine[1)]

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The di- and trisaccharide sequences and their conjugates with serine recently identified in the first epidermal growth factor-like domain of bovine and human blood-clotting factors VII, IX, and protein Z were synthesized in order to elucidate their biological function. The disaccharide α-D-Xyl*p*(1→3)-D-Glc*p* was prepared from 2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl fluoride and allyl 2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (**9a**) using tin(II) chloride and silver perchlorate as glycosylating reagents. The trisaccharide α-D-Xyl*p*(1→3)-α-D-Xyl*p*(1→3)-D-Glc*p* was prepared from *O*-(2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-2,4-di-*O*-benzyl-α,β-D-xylopyranosyl fluoride and **9a** with the same reagents. Their conjugates with serine, α-D-Xyl*p*(1→3)-β-D-Glc*p*(1→3)-L-Ser and α-D-Xyl*p*(1→3)-α-D-Xyl*p*(1→3)-β-D-Glc*p*(1→3)-L-Ser, were synthesized by the glycosylation of *N*-benzyloxycarbonyl-L-serine benzyl ester with the corresponding glycosyl trichloroacetimidates of the above saccharides, followed by removal of the protecting groups. The *p*-nitrobenzyl group, which was recently devised for temporary protection of hydroxyl functions, was used for the 3-hydroxyl group of glucose.

Blood-clotting factors VII and IX are the plasma glycoproteins that participate in the pathway of the blood coagulation cascade.[2,3)] Protein Z is a vitamin K-dependent protein of unknown function recently isolated from human and bovine plasmas.[4–7)] These proteins are synthesized in the liver and undergo specific posttranslational modifications prior to secretion.

Recently, a new type of serine-linked saccharides were found in the first epidermal growth factor (EGF)-like domain of bovine and human factors VII (Ser-52) and IX (Ser-53) and protein Z (Ser-53).[8,9)] Bovine proteins have a trisaccharide composed of 1 mol of glucose (Glc) and 2 mol of xylose (Xyl). The trisaccharide of bovine factor IX was identified as α-D-Xyl*p*(1→3)-α-D-Xyl*p*(1→3)-D-Glc*p* (**3**), and bound to serine 53 by β-D-linkage as shown in Fig. 1.[10)] Bovine factor VII and protein Z have the same trisaccharide. In the corresponding human proteins, the above trisaccharide and/or a disaccharide whose structure was proposed to be α-D-Xyl*p*-(1→3)-D-Glc*p* (**1**) are located at the same position indicating microheterogeneity of these *O*-linked sugar chains. The functional role of these sugar chains for the activities of the above proteins is still unknown. However, some biological roles are anticipated in protein–protein or protein–cell interactions, since the amino acid sequences surrounding the particular serine residue that links to these saccharides are considered to be located on the surface of the proteins.[8,9)] In the present study, we carried out the synthesis of the above oligosaccharides and their conjugates with serine for the confirmation of the proposed structure as well as for the elucidation of its biological significance.

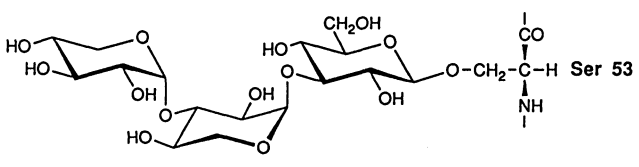


Fig. 1. Proposed structure for the trisaccharide linked to the serine 53 residue of bovine factor IX.

Results and Discussion

For the preparation of α-D-glycosidic linkage between the sugar components, we employed Mukaiyama's procedure[11)] using glycosyl fluoride as a donor, and tin(II) chloride and silver perchlorate as glycosylating reagents, whereas the condensation of sugar components with the serine residue in β-linkage was carried out using glycosyl trichloroacetimidates as donors in the presence of boron trifluoride etherate as a catalyst.[12)]

The outline of the synthesis is as follows. The disaccharide α-D-Xyl*p*(1→3)-D-Glc*p* (**1**) was prepared by reaction of 2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl fluoride (**10**)[13)] with allyl 2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (**9a**) followed by successive deprotection of the resultant disaccharide **11a**. α-D-Xyl*p*(1→3)-β-D-Glc*p*(1→3)-L-Ser (**2**) was prepared via the glycosylation of *N*-benzyloxycarbonyl-L-serine benzyl ester (Z-Ser-OBzl) (**17**) with the disaccharide trichloroacetimidate (**16**). The trisaccharide, α-D-Xyl*p*(1→3)-α-D-Xyl*p*-(1→3)-D-Glc*p*(**3**), was prepared from *O*-(2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-2,4-di-*O*-benzyl-α,β-D-xylopyranosyl fluoride (**23**) and allyl glucoside acceptor **9a**. The serine conjugate of the trisaccharide, α-D-Xyl*p*(1→3)-α-D-Xyl*p*(1→3)-β-D-Glc*p*(1→3)-L-Ser (**4**), was synthesized by the same procedure as the prepara-

tion of **2**.

Thus, we first prepared the acceptor **9a** by use of the *p*-nitrobenzyl (NPM) group for temporary protection of the 3-position. In spite of its strong stability to acid, NPM group has been seldom used for the protection of hydroxyl functions until recently because of the lack of other particular advantages over the simple benzyl group. However, we recently found NPM group can be removed selectively in the presence of other hydroxyl protecting groups such as the benzyl group. After selective catalytic hydrogenation of the nitro group of the NPM ether, the resulting 4-aminobenzyl group can be selectively removed either by electrochemical oxidation or by 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) oxidation after *N*-acetylation.[14]

Diisopropylideneglucose **5** was *p*-nitrobenzylated with NPM bromide and silver oxide in benzene[15] to give compound **6** in 91% yield, which was treated with HCl–allyl alcohol and then with acetic anhydride and pyridine to give α- and β-allyl glucoside **7a** (62%) and **7b** (14%). Reduction of the nitro group was then examined for the selective cleavage of NPM group in **7a**. Among the reducing methods tested, we found a combination of zinc–copper couple and acetylacetone reduces the nitro group quite smoothly at room temperature without any change of the allyl group.[16] The resulting aminobenzyl group was then acetylated with acetic anhydride to give 4-acetamidobenzyl ether **8a** (93%). DDQ oxidation of **8a** proceeded smoothly to give the desired glycosyl acceptor **9a** in 94% yield.

We then synthesized α-D-Xyl*p*(1→3)-D-Glc*p* (**1**) and α-D-Xyl*p*(1→3)-β-D-Glc*p*(1→3)-L-Ser (**2**) as shown in Scheme 1. 2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl fluoride (**10**) was coupled with α-allyl glucoside **9a**[17] in ether at −10 °C in the presence of tin(II) chloride and silver perchlorate. The desired α-disaccharide **11a** and its β anomer **11b** were obtained with no selectivity (α : β=1 : 1)[18] in total 96% yield. Since **11a** and **11b** were not separable by silica-gel column chromatography, the allyl group of **11a** and **11b** was then isomerized using an iridium complex[19] to give 1-propenyl glycosides **12a** and **12b** in 88% yield, which were also difficult to separate by either silica-gel column chromatography or high-performance liquid chromatography (HPLC) on a reversed-phase column (Cosmosil 5C18 AR, Nacalai Tesque). Therefore, compounds **12a** and **12b** were further deacetylated to increase the hydrophilicity for better separation on a reversed-phase column. Indeed, deacetylated α-anomer **13a** (47%) was separated effectively from the β-anomer **13b** (41%) by HPLC (Cosmosil 5C18 AR). 1-Propenyl group of **13a** was then removed with iodine[20] to give **14** (82%). Catalytic hydrogenolysis of **14** afforded the desired disaccharide α-D-Xyl*p*(1→3)-D-Glc*p* (**1**) in 89% yield.

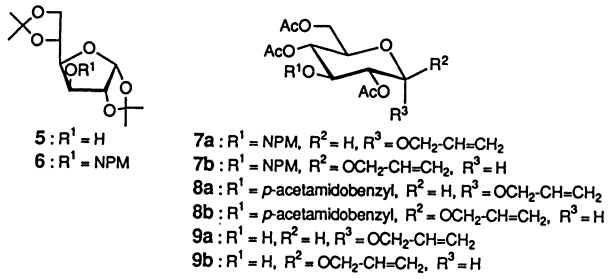
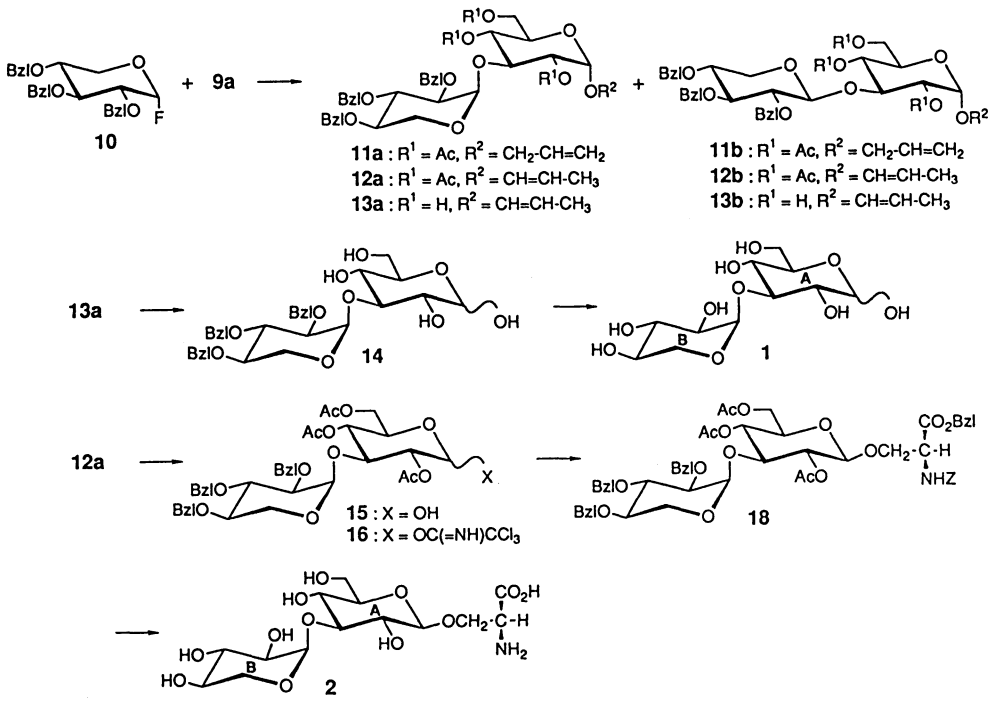


Fig. 2.

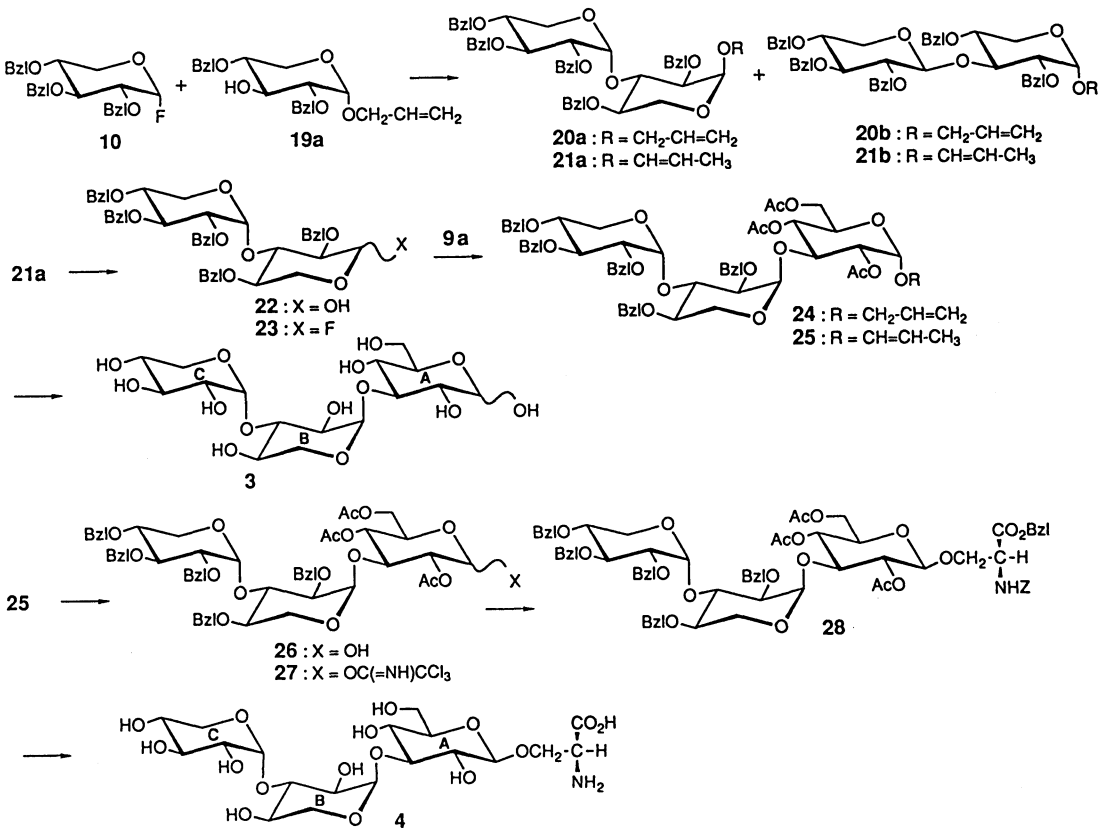


Scheme 1.

For the preparation of α-D-Xyl*p*(1→3)-β-D-Glc*p* (1→3)-L-Ser (**3**), compound **13a** was acetylated again to give pure **12a** (99%), which was then treated with iodine to give the disaccharide **15** with free 1-hydroxyl group (82%). Compound **15** was allowed to react with trichloroacetonitrile in the presence of Cs_2CO_3 as the catalyst to give trichloroacetimidate **16** as a 2:1 mixture of the α- and β-anomers in quantitative yield.[21] Condensation of **16** with Z-Ser-OBzl (**17**) was then carried out using boron trifluoride etherate as the catalyst to give a protected diglycosyl serine **18** in 66% yield. Desired α-D-Xyl*p*(1→3)-β-D-Glc*p*(1→3)-L-Ser (**2**) was obtained by catalytic hydrogenolysis of **18** and subsequent hydrazinolysis[22] in 59% yield.

We then carried out the synthesis of the trisaccharide α-D-Xyl*p*(1→3)-α-D-Xyl*p*(1→3)-D-Glc*p* (**3**) and its serine conjugate α-D-Xyl*p*(1→3)-α-D-Xyl*p*(1→3)-β-D-Glc*p*-(1→3)-L-Ser (**4**) as shown in Scheme 2. Since no α-selectivity was observed at the glycosylation of α-allyl glucoside **9a** with 2,4-di-*O*-benzyl-3-*O*-(*p*-nitrobenzyl)-α-D-xylopyranosyl fluoride (α:β=1:1), and since the anomers of the resulting disaccharide were separable at all by neither silica-gel column chromatography nor HPLC in the preliminary experiments, we examined another route for preparation of the trisaccharide. The reaction of xylosyl fluoride **10** with allyl 2,4-di-*O*-benzyl-α-D-xylopyranoside (**19a**)[23] proceeded smoothly to give α-anomer **20a** preferentially as a mixture with β-anomer **20b** (α:β=1:0.6)[13] in total 85% yield. Although **20a** and **20b** could not be separated, the 1-propenyl glycosides, after isomerization of the allyl group, were separated effectively by silica-gel column chromatography to give **21a** and **21b** in 53% and 30% yields, respectively. Cleavage of the 1-propenyl group of **21a** and subsequent reaction using 2-fluoro-1-methylpyridinium *p*-toluenesulfonate and triethylamine[24] gave fluoride **23** as a 3.2:1 mixture of the α- and β-anomers in 77% yield. The fluoride **23** was then coupled with the allyl glucoside **9a** to give the α-linked trisaccharide **24a** (72%) preferentially (α:β=3.7:1). The allyl group of compound **24a** was isomerized by the iridium complex to give **25** in 96% yield. Successive removal of the acetyl, 1-propenyl, and benzyl groups in **25** afforded the free trisaccharide α-D-Xyl*p*(1→3)-α-D-Xyl*p*(1→3)-D-Glc*p* (**3**) in 62% yield. The oligoglycosyl serine, α-D-Xyl*p*(1→3)-α-D-Xyl*p*(1→3)-β-D-Glc*p*(1→3)-L-Ser (**4**), could be also synthesized from trisaccharide **25** by the same procedure as described for the preparation of α-D-Xyl*p*(1→3)-β-D-Glc*p*(1→3)-L-Ser (**2**). Thus, removal of the 1-propenyl group of **25** followed by a reaction with trichloroacetonitrile gave **27** in 94% yield. The glycosylation of Z-Ser-OBzl (**17**) with **27** gave **28** in 66% yield. The final removal of all the protecting groups of compound **28** afforded the desired triglycosyl serine **4** in 54% yield.

All of the above oligosaccharides, **1** and **3**, and their conjugates with Ser, **2** and **4**, were effectively purified by HPLC on a reversed phase column (Cosmosil 5C18 AR)



Scheme 2.

Table 1. ^{1}H NMR Data for Compounds **1**, **2**, **3**, and **4**[a]

H-atom[b]	Chemical shifts (δ)						Coupling constants (Hz)						
	1a[c]	**1b**[d]	**3a**[e]	**3b**[f]	**2**	**4**	J_{H-H}	**1a**	**1b**	**3a**	**3b**	**2**	**4**
1_A	5.21	4.64	5.22	4.64	4.49	4.50	1_A–2_A	3.8	8.1	3.8	8.1	8.0	8.0
2_A	3.61	3.32	3.62	3.33	3.42	3.43	2_A–3_A	Nd[g]	8.6	Nd	8.8	9.5	9.2
3_A	3.82	3.60	3.82	3.60	3.60	3.61	3_A–4_A	Nd	Nd	Nd	Nd	Nd	Nd
4_A	3.62	3.62	3.62	3.62	3.65	3.66	4_A–5_A	Nd	9.4	Nd	9.6	Nd	Nd
5_A	3.83	3.45	3.84	3.45	3.44	3.45	5_A–6_A	5.3	5.8	Nd	5.8	5.9	5.8
6_A	3.74	3.69	3.74	3.70	3.70	3.71	5_A–$6'_A$	Nd	2.4	Nd	2.2	2.2	2.2
$6'_A$	3.81	3.86	3.81	3.86	3.89	3.89	5_A–$6'_A$	12.5	12.4	Nd	Nd	12.4	12.5
1_B	5.32	5.31	5.32	5.31	5.29	5.30	1_B–2_B	3.8	3.5	2.6	3.7	3.8	3.7
2_B	3.54	3.53	3.66	3.66	3.53	3.66	2_B–3_B	9.5	9.5	Nd	Nd	9.3	Nd
3_B	3.67	3.67	3.80	3.80	3.66	3.80	3_B–4_B	Nd	Nd	Nd	Nd	Nd	Nd
4_B	3.60	3.60	3.81	3.81	3.59	3.81	4_B–5_{eqB}	Nd	Nd	Nd	Nd	Nd	Nd
5_{eqB}	3.65	3.65	3.65	3.65	3.64	3.64	4_B–5_{axB}	Nd	Nd	Nd	Nd	10.3	Nd
5_{axB}	3.85	3.85	3.84	3.84	3.86	3.85	5_{eqB}–5_{axB}	Nd	Nd	Nd	Nd	10.3	Nd
1_C			5.30	5.30		5.29	1_C–2_C			3.8	3.8		3.8
2_C			3.53	3.53		3.53	2_C–3_C			9.6	9.6		9.7
3_C			3.67	3.67		3.67	3_C–4_C			Nd	Nd		Nd
4_C			3.59	3.59		3.59	4_C–5_{eqC}			Nd	Nd		Nd
5_{eqC}			3.65	3.65		3.65	4_C–5_{axC}			Nd	Nd		Nd
5_{axC}			3.84	3.84		3.85	5_{eqC}–5_{axC}			Nd	Nd		Nd
Ser2					3.98	3.98	Ser2–Ser3					3.3	3.3
Ser3					4.06	4.06	Ser2–Ser3′					5.8	5.8
Ser3′					4.29	4.29	Ser3–Ser3′					11.4	11.4

a) at 400 MHz, in D_2O, 30 °C. b) Subscripts A, B, and C refer to individual monosaccharide units as shown in Schemes 1 and 2. c) **1a**: α-D-Xyl*p*(1→3)-α-D-Glc*p*. d) **1b**: α-D-Xyl*p*(1→3)-β-D-Glc*p*. The ratio of **1a** and **1b** in D_2O was 1 : 1.4. e) **3a**: α-D-Xyl*p*(1→3)-α-D-Xyl*p*(1→3)-α-D-Glc*p*. f) **3b**: α-D-Xyl*p*(1→3)-α-D-Xyl*p*(1→3)-β-D-Glc*p*. The ratio of **3a** and **3b** in D_2O was 1 : 1.4. g) Nd: not determined.

Table 2. ^{13}C NMR Data for Compounds **1**, **2**, **3**, and **4**[a]

C-atom	Chemical shifts (δ)					
	1a	**1b**	**3a**	**3b**	**2**	**4**
1_A	93.1	96.8	93.1	96.8	103.0	103.0
2_A	70.9	73.6	Nd[b]	73.6	72.41	72.4
3_A	80.2	82.7	80.4	82.9	82.5	82.7
4_A	71.0	71.0	Nd[b]	Nd[b]	70.8	70.7
5_A	72.1	76.5	72.1	76.5	76.5	76.5
6_A	61.2	61.4	61.2	61.4	61.3	61.3
1_B	100.0	99.8	100.1	100.0	99.9	100.0
2_B	72.52	72.49	Nd[b]	Nd[b]	72.44	70.9
3_B	73.9	73.9	80.0	80.0	73.8	80.0
4_B	70.2	70.2	70.5	70.5	70.2	70.6
5_B	62.3	62.3	62.4	62.4	62.3	62.5
1_C			99.8	99.8		99.8
2_C			72.5	72.5		72.5
3_C			73.9	73.9		73.9
4_C			70.2	70.2		70.2
5_C			62.3	62.3		62.3
Ser1					172.4	172.4
Ser2					55.5	55.5
Ser3					68.7	68.7

a) At 100.4 MHz, in D_2O, 30 °C. b) The chemical shifts of these carbon atoms could not be determined becauese the signals appeared very close to each other (70.87, 70.91, and 70.97 ppm).

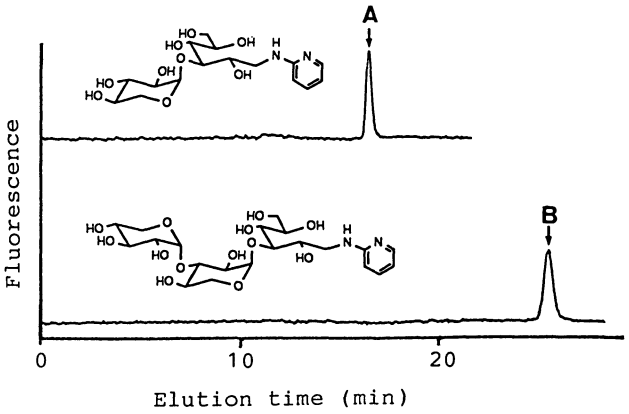


Fig. 3. HPLC of pyridylamino derivatives of synthetic α-D-Xylp(1→3)-D-Glc*p* (**1**) and α-D-Xyl*p*(1→3)-α-D-Xyl*p*(1→3)-D-Glc*p* (**3**). PA-oligosaccharides were analyzed by reversed-phase HPLC with a Cosmosil 5C18-P column (10×250 mm) and 0.1 M ammonium acetate buffer, pH 4.0 at the flow rate 4.0 ml min^{-1}, and were detected by fluorescence using an excitation wavelength of 320 nm and an emission wavelength 400 nm. The arrow A indicates the elution position of α-D-Xyl*p*(1→3)-D-Glc-PA obtained from human blood-clotting factor IX; B, α-D-Xyl*p*(1→3)-α-D-Xyl*p*(1→3)-D-Glc-PA obtained from bovine blood clotting factor IX.

using H_2O as an eluent. The structure and the purity of each product were confirmed by elemental analysis, FAB-mass spectra, and ^{1}H and ^{13}C NMR spectra, where proton and carbon signals were unambiguously assigned by analysis of the H–H and C–H COSY spectra as shown in Table 1 and Table 2, respectively. The pyridylamino (PA) derivatives[25] of both synthetic disaccha-

ride **1** and trisaccharide **3** were identical with those of natural **1** and **3**, respectively, obtained from human and bovine blood-clotting factor IX[8-10] on reversed-phase HPLC (Cosmosil 5C18-P, Nacalai Tesque) as shown in Fig. 3. ^{1}H NMR spectrum (500 MHz) of synthetic PA-trisaccharide[10] was also identical with that of natural one. The biological role of these carbohydrate chains in the first EGF-like domain is now being investigated.

Experimental

All melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained with a JEOL JNM-GSX 270, 400, or 500 spectrometer. The chemical shifts are given in δ values either from TMS as the internal standard in $CDCl_3$ solutions or from sodium 2,2-dimethyl-2-silapentane-5-sulfonate as the external standard in D_2O solutions. FAB-MS spectra were obtained with a JEOL SX-102 mass spectrometer. Specific rotations were obtained with a Perkin-Elmer 241 polarimeter. HPLC was carried out with a Shimadzu LC-6AD liquid chromatograph. Silica-gel column chromatography was carried out with Merck silica gel 60 (230—400 mesh) at medium pressure (2—10 kg cm^{-2}). Organic solutions were dried over $MgSO_4$ and evaporated in vacuo. Pyridylamino (PA) derivatives of oligosaccharides were prepared as described previously[25] and analyzed by reversed-phase HPLC with a Beckman model 344 M chromatograph with a Cosmosil 5C18-P (Nacalai Tesque) column [10×250 mm; solvent: 0.1 M ammonium acetate buffer (1 M=1 mol dm^{-3}), pH 4.0; flow rate: 4.0 ml min^{-1}]: the peaks were detected with a Hitachi model F-3000 fluorescence spectrophotometer by using an excitation wavelength of 320 nm and an emission wavelength of 400 nm.

1,2;5,6-Di-*O*-isopropyridene-3-*O*-(*p*-nitrobenzyl)-α-D-glucofuranose (6). To a suspension of 1,2;5,6-di-*O*-isopropyridene-α-D-glucofuranose (**5**) (15.0 g, 57.7 mmol) in benzene (150 ml) were added *p*-nitrobenzyl bromide (16.2 g, 75.0 mmol), Ag_2O (17.4 g, 75.0 mmol), and molecular sieves 3A (15 g). The mixture was stirred at room temperature for 2 d. After the mixture was filtered, the filtrate was concentrated. The residue was purified by silica-gel column chromatography (160 g, 3×50 cm, toluene–AcOEt=10 : 1) to give an oily product: Yield 20.8 g (91.2 %); $[\alpha]_D^{22}$ −35.2° (*c* 1.60, $CHCl_3$). Found: C, 57.62; H, 6.18; N, 3.54%. Calcd for $C_{19}H_{25}O_8N$: C, 57.71; H, 6.37; N, 3.54%.

Allyl 2,4,6-Tri-*O*-acetyl-3-*O*-(*p*-nitrobenzyl)-α-D-glucopyranoside (7a) and Allyl 2,4,6-Tri-*O*-acetyl-3-*O*-(*p*-nitrobenzyl)-β-D-glucopyranoside (7b). A solution of compound **6** (12.0 g, 30.4 mmol) in 4% HCl–allyl alcohol (90 ml) was refluxed for 20 min and then concentrated to give a solid, which was then dissolved in Ac_2O (70 ml, 0.74 mol) and pyridine (70 ml, 0.87 mol). The mixture was stirred at room temperature for 4 h and then concentrated. Compound **7a** and **7b** were separated by silica-gel column chromatography (160 g, 3×50 cm, benzen–AcOEt=9 : 1).

7a: Yield 9.00 g (61.6%); mp 76—78 °C; $[\alpha]_D^{22}$ +64.9° (*c* 0.835, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.99 (3H, s, Ac), 2.05 (3H, s, Ac), 2.10 (3H, s, Ac), 3.96 (1H, ddd, *J*=2.5, 5.0, 9.3 Hz, H-5), 4.0—4.25 (2H, m, $OC\underline{H}_2CH{=}CH_2$), 4.04 (1H, dd, *J*=10.1, 10.1 Hz, H-3), 4.09 (1H, dd, *J*=2.5, 12.4 Hz, H-6), 4.22 (1H, dd, *J*=5.0, 12.4 Hz, H-6′), 4.73 (1H, d, *J*=13.2 Hz, $C\underline{H}_2C_6H_4NO_2$), 4.84 (1H, d, *J*=13.2 Hz, $C\underline{H}_2C_6H_4NO_2$), 4.91 (1H, dd, *J*=3.8, 10.1 Hz, H-2), 5.12 (1H, d, *J*=3.8 Hz, H-1), 5.14 (1H, dd, *J*=9.3, 10.1 Hz, H-4), 5.25 (1H, m, $OCH_2CH{=}C\underline{H}_2$), 5.31 (1H, m, $OCH_2CH{=}C\underline{H}_2$), 5.89 (1H, m, $OCH_2C\underline{H}{=}CH_2$), 7.42 (2H, m, *m*-$C_6\underline{H}_4NO_2$), 8.18 (2H, m, *o*-$C_6\underline{H}_4NO_2$). Found: C, 54.91; H, 5.67; N, 2.89%. Calcd for $C_{22}H_{27}O_{11}N$: C, 54.88; H, 5.65; N, 2.91%.

7b: Syrup, yield 2.10 g (14.4 %); $[\alpha]_D^{22}$ −15.3° (*c* 0.695, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ=2.02 (3H, s, Ac), 2.03 (3H, s, Ac), 2.08 (3H, s, Ac), 3.65 (1H, ddd, *J*=2.7, 5.2, 9.9 Hz, H-5), 3.77 (1H, dd, *J*=9.3, 9.3 Hz, H-3), 4.0—4.4 (4H, m, H-6, H-6′, $OC\underline{H}_2CH{=}CH_2$) 4.52 (1H, d, *J*=7.9 Hz, H-1), 4.74 (2H, s, $C\underline{H}_2C_6H_4NO_2$), 5.08—5.30 (4H, m, H-2, H-4, $OCH_2CH{=}C\underline{H}_2$), 5.85 (1H, m, $OCH_2C\underline{H}{=}CH_2$), 7.42 (2H, m, *m*-$C_6\underline{H}_4NO_2$), 8.16 (2H, m, *o*-$C_6\underline{H}_4NO_2$). Found: C, 54.54; H, 5.77; N, 2.72%. Calcd for $C_{22}H_{27}O_{11}N$: C, 54.88; H, 5.65; N, 2.91%.

Allyl 2,4,6-Tri-*O*-acetyl-3-*O*-(*p*-acetamidobenzyl)-α-D-glucopyranoside (8a). To a solution of compound **7a** (13.1 g, 27.2 mmol) in THF (200 ml) and acetylacetone (100 ml, 0.98 mol) was added Zn–Cu couple (20 g). The mixture was stirred at 0 °C for 30 min and then filtered. To the filtrate was added Ac_2O (12.5 ml, 132 mmol), and the mixture was allowed to stand at room temperature for 10 min, and then concentrated. After addition of AcOEt (75 ml) and hexane (75 ml) to the residue, insoluble material was filtered off. The residue obtained by evaporation of the solvent was purified by silica-gel column chromatography (160 g, 3×50 cm, benzene–AcOEt=1 : 1) to give a crystalline product: Yield 12.5 g (93.3%); mp 131—135 °C; $[\alpha]_D^{22}$ +65.1° (*c* 1.13, $CHCl_3$). Found: C, 58.36; H, 6.38; N, 2.80%. Calcd for $C_{24}H_{31}O_{10}N$: C, 58.41; H, 6.33; N, 2.84%.

Allyl 2,4,6-Tri-*O*-acetyl-α-D-glucopyranoside (9a). To a solution of compound **8a** (12.0 g, 24.3 mmol) in CH_2Cl_2 (160 ml) and water (8 ml) was added DDQ (6.63 g, 29.2 mmol). The mixture was stirred at room temperature for 1 h and then filtered. The filtrate was washed with water, and worked up as usual. The residue was purified by silica-gel column chromatography (170 g, 3×53 cm, benzene–AcOEt=2 : 1) to give a crystalline product: Yield 7.92 g (94.0%); mp 72—75 °C; $[\alpha]_D^{22}$ +117° (*c* 1.21, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ=2.10 (3H, s, Ac), 2.12 (3H, s, Ac), 2.14 (3H, s, Ac), 2.18 (1H, bs, OH), 3.98 (1H, ddd, *J*=2.5, 4.7, 10.0 Hz, H-5), 4.00—4.22 (4H, m, H-3, H-6, $OC\underline{H}_2CH{=}CH_2$), 4.27 (1H, dd, *J*=4.7, 12.2 Hz, H-6′), 4.78 (1H, dd, *J*=3.7, 9.9 Hz, H-2), 4.94 (1H, dd, *J*=9.8, 10.0 Hz, H-4), 5.08 (1H, d, *J*=3.7 Hz, H-1), 5.22 (1H, m, $OCH_2CH{=}C\underline{H}_2$), 5.31 (1H, m, $OCH_2CH{=}C\underline{H}_2$), 5.89 (1H, m, $OCH_2C\underline{H}{=}CH_2$). Found: C, 52.01; H, 6.41%. Calcd for $C_{15}H_{22}O_9$: C, 52.02; H, 6.40%.

Allyl 2,4,6-Tri-*O*-acetyl-3-*O*-(*p*-acetamidobenzyl)-β-D-glucopyranoside (8b).[16] A mixture of compound **7b** (1.70 g, 3.53 mmol), Zn–Cu couple (9.8 g), and $CaCl_2$ (392 mg, 3.53 mmol) in MeOH (34 ml) was refluxed for 4 h, filtered, and then concentrated. The residue was dissolved in Ac_2O (30 ml, 0.32 mol) and pyridine (30 ml, 0.37 mol). The mixture was allowed to stand at room temperature overnight, and then concentrated. The residue was purified by silica-gel column chromatography (40 g, 1.5×50 cm, $CHCl_3$–MeOH=30 : 1) to give a crystalline product: Yield 1.65 g (94.8%); mp 96—100 °C; $[\alpha]_D^{22}$ −21.0° (*c* 1.13, $CHCl_3$). Found: C, 57.77; H, 6.40; N, 2.89%. Calcd for $C_{24}H_{31}O_{10}N \cdot 0.3\ H_2O$: C, 57.77; H, 6.38; N, 2.81%.

Allyl 2,4,6-Tri-*O*-acetyl-β-D-glucopyranoside (9b). *p*-Acetamidobenzyl group in compound **8b** (1.55 g, 3.14 mmol) was removed with DDQ (784 mg, 3.45 mmol) in CH_2Cl_2 (20

ml) and water (4 ml) as described for the preparation of **9a**. The crude product was purified by silica-gel column chromatography (70 g, 2×45 cm, $CHCl_3$–MeOH=50 : 1) to give an oily product: Yield 767 mg (70.4%); $[\alpha]_D^{22}$ −39.0° (*c* 1.14, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ=2.09 (3H, s, Ac), 2.11 (3H, s, Ac), 2.13 (3H, s, Ac), 3.62 (1H, ddd, *J*=2.5, 4.9, 9.7 Hz, H-5), 3.71 (1H, dd, *J*=9.7, 9.7 Hz, H-3), 4.05—4.37 (4H, m, H-6, H-6′, $OC\underline{H}_2CH{=}CH_2$) 4.50 (1H, d, *J*=7.9 Hz, H-1), 4.87 (1H, dd, *J*=7.9, 9.6 Hz, H-2), 4.95 (1H, dd, *J*=9.7, 9.7 Hz, H-4) 5.85 (1H, m, $OCH_2C\underline{H}{=}CH_2$). Found: C, 52.34; H, 6.45%. Calcd for $C_{15}H_{22}O_9$: C, 52.02; H, 6.40%.

Allyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (11a) and Allyl *O*-(2,3,4-Tri-*O*-benzyl-β-D-xylopyranosyl)-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (11b). To a mixture of compound **9a** (2.05 g, 5.92 mmol), $SnCl_2$ (1.23 g, 6.51 mmol), $AgClO_4$ (1.35 g, 6.51 mmol), and powdered molecular sieves 4A (10 g) in ether (80 ml) was added a solution of 2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl fluoride (**10**)[13] (2.50 g, 5.92 mmol) in ether (40 ml) at −10 °C. After the mixture had been stirred at −10 °C overnight, saturated $NaHCO_3$ solution was added and the mixture was filtered. The organic layer was separated, and worked up as usual. The residue was purified by silica-gel column chromatography (70 g, 2×45 cm, benzene–AcOEt=10 : 1) to give an oily product as a 1 : 1 mixture (4.25 g, 95.9%) of **11a** and **11b**; ^1H NMR (270 MHz, $CDCl_3$) δ=1.81 (1.5H, s, Ac), 1.84 (1.5H, s, Ac), 2.00 (1.5H, s, Ac), 2.06 (1.5H, s, Ac), 2.100 (1.5H, s, Ac), 2.104 (1.5H, s, Ac), 3.18 (0.5H, dd, *J*=9.5, 11.5 Hz, $H_B\beta$-5ax), 3.28 (0.5H, dd, *J*=7.7, 8.9 Hz, $H_B\beta$-2), 3.33 (0.5 H, dd, *J*=3.2, 9.6 Hz, $H_B\alpha$-2), 3.4—4.3 (9.5H, m), 4.45 (0.5H, d, *J*=7.7 Hz, $H_B\beta$-1), 4.55—5.36 (11.5H, m), 5.88 (1H, m, $OCH_2C\underline{H}{=}CH_2$), 7.2—7.4 (15H, m, $CH_2C_6\underline{H}_5$×3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=95.0, 95.3 ($C_A\alpha$-1, $C_A\beta$-1), 98.8 ($C_B\alpha$-1), 104.3 ($C_B\beta$-1). Found: C, 63.30; H, 6.40%. Calcd for $C_{41}H_{48}O_{13}\cdot 1.5H_2O$: C, 63.47; H, 6.63%.

1-Propenyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (12a) and 1-Propenyl *O*-(2,3,4-Tri-*O*-benzyl-β-D-xylopyranosyl)-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranonide (12b). To a solution of the mixture of **11a** and **11b** (4.25 g, 5.68 mmol) in THF (100 ml) was added $[Ir(COD)(PMe(C_6H_5)_2)_2]PF_6$ (110 mg, 0.130 mmol) under N_2 atmosphere. The N_2 in the system was replaced with H_2, and the solution was stirred at room temperature for 1 min. The system was evacuated until the color of the solution changed from yellow to light red, and then filled again with N_2. The solution was stirred at 50 °C for 20 min and then concentrated. The residue was purified by silica-gel column chromatography (70 g, 2×45 cm, benzene–AcOEt=10 : 1) to give an oily product as a 1 : 1 mixture (3.72 g, 87.5%) of **12a** and **12b**; ^1H NMR (270 MHz, $CDCl_3$) δ=1.56 (3H, m, OCH=CH–$C\underline{H}_3$), 1.81 (1.5H, s, Ac), 1.84 (1.5H, s, Ac), 2.00 (1.5H, s, Ac), 2.06 (1.5H, s, Ac), 2.088 (1.5H, s, Ac), 2.091 (1.5H, s, Ac), 3.18 (0.5H, dd, *J*=9.5, 11.5 Hz, $H_B\beta$-5ax), 3.28 (0.5H, dd, *J*=7.7, 8.9 Hz, $H_B\beta$-2), 3.33 (0.5H, dd, *J*=3.3, 9.8 Hz, $H_B\alpha$-2), 3.4—4.25 (7.5H, m), 4.45 (0.5H, d, *J*=7.7 Hz, $H_B\beta$-1), 4.55—5.30 (10.5H, m), 6.12 (1H, m, $OC\underline{H}$=CH–CH_3), 7.2—7.4 (15H, m, $CH_2C_6\underline{H}_5$×3). Found: C, 65.91; H, 6.39%. Calcd for $C_{41}H_{48}O_{13}$: C, 65.76; H, 6.46%.

1-Propenyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-α-D-glucopyranoside (13a). A solution of the mixture of **12a** and **12b** (3.60 g, 4.81 mmol) in 0.04 M MeONa solution (120 ml) was stirred at room temperature for 2 h and then neutralized with Dry Ice. After the mixture was concentrated, the residue was dissolved in AcOEt, washed with brine, and worked up as usual. The residue was purified by HPLC [column: Cosmosil 5C18 AR (Nacalai Tesque), 20×250 mm; solvent: 73% CH_3CN–H_2O; flow rate: 9.0 ml min^{-1}; detection: UV at 240 nm] to give **13a** (retention time: 10.6 min) and 1-propenyl *O*-(2,3,4-tri-O-benzyl-β-D-xylopyranosyl)-(1→3)-α-D-glucopyranoside (**13b**) (retention time: 12.4 min) as oily products.

13a: Yield 1.40 g (46.8%); $[\alpha]_D^{20}$ +100° (*c* 1.14, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ=1.56 (3H, dd, *J*=1.7, 6.9 Hz, OCH=CH–$C\underline{H}_3$), 3.50 (1H, dd, 3.7, 9.7 Hz, H_B-2), 3.5—4.0 (11H, m), 4.80 (1H, d, *J*=3.7 Hz, H_B-1), 4.5—5.0 (6H, m, $C\underline{H}_2C_6H_5$×3), 5.11 (1H, d, *J*=3.5 Hz, H_A-1), 5.19 (1H, m, *J*=6.9, 12.4 Hz, OCH=C$\underline{H}$–CH_3), 6.18 (1H, m, *J*=1.7, 12.4 Hz, $O\underline{C}H$=CH–CH_3), 7.2—7.4 (15H, m, $CH_2C_6\underline{H}_5$×3); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=12.4 (OCH=CH–$\underline{C}H_3$), 61.0, 62.5 (C_A-6, C_B-5), 70.3, 70.8, 71.3, 73.5, 74.5, 75.7, 78.0, 79.2, 81.5, 86.8, (C_A-2,3,4,5, C_B-2,3,4, $\underline{C}H_2C_6H_5$×3), 98.0 (C_A-1), 100.8 (C_B-1), 105.4 (OCH=$\underline{C}$H–CH_3), 127.6—128.7 (aromatic CH), 137.2, 138.1, 138.6 (aromatic C×3), 142.7 ($O\underline{C}$H=CH–CH_3). Found: C, 66.62; H, 6.68%. Calcd for $C_{35}H_{42}O_{10}\cdot 0.5H_2O$: C, 66.74; H, 6.85%.

13b: Yield 1.24 g (41.5%); $[\alpha]_D^{24}$ +44.9° (*c* 0.675, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ=1.56 (3H, dd, *J*=1.7, 6.9 Hz, OCH=CH$C\underline{H}_3$), 3.2—4.0 (12H, m), 4.47 (1H, d, *J*=7.7 Hz, H_B-1), 4.58—4.95 (6H, m, $C\underline{H}_2C_6H_5$×3), 5.07 (1H, d, *J*=3.7 Hz, H_A-1), 5.17 (1H, m, *J*=6.9, 12.4 Hz, OCH=C$\underline{H}$–CH_3), 6.16 (1H, m, *J*=1.7, 12.4 Hz, $O\underline{C}H$=CH–CH_3), 7.2—7.4 (15H, m, $CH_2C_6\underline{H}_5$×3). Found: C, 64.86; H, 6.86%. Calcd for $C_{35}H_{42}O_{10}\cdot 1.4H_2O$: C, 64.88; H, 6.97%.

***O*-(2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-D-glucopyranose (14).** To a solution of **13a** (306 mg, 0.491 mmol) in THF (9 ml) and water (3 ml) was added I_2 (249 mg, 0.982 mmol) in THF (3ml). The solution was stirred at room temperature for 1 h, and a 5% $Na_2S_2O_3$ solution was added until the color of I_2 disappeared. AcOEt and a saturated $NaHCO_3$ solution were added to the mixture. The organic layer separated was washed with brine and worked up as usual. The residue was purified by HPLC [column: Cosmosil 5C18 (Nacalai Tesque), 16.7×250 mm; solvent: CH_3CN–H_2O, gradient: 55—90% (2% min^{-1}); flow rate: 8.0 ml min^{-1}; detection: UV at 240 nm] to give an oily product: Yield 320 mg (82.3%); $[\alpha]_D^{20}$ +64.5° (*c* 1.07, $CHCl_3$). Found: C, 64.31; H, 6.66%. Calcd for $C_{32}H_{38}O_{10}\cdot 0.8H_2O$: C, 64.37; H, 6.69%.

***O*-α-D-Xylopyranosyl-(1→3)-D-glucopyranose (1).** Compound **14** (286 mg, 0.491 mmol) was hydrogenated in MeOH (20 ml) with Pd-black (200 mg) at room temperature under 6.5 kg cm^{-2} of H_2 overnight. The catalyst was filtered off, and the filtrate was concentrated. The residue was purified by HPLC (column: Cosmosil 5C18 AR, 20×250 mm; solvent: H_2O; flow rate: 8.0 ml min^{-1}), and lyophilyzed to give **1** as a powder: Yield 137 mg (89.3 %); $[\alpha]_D^{22}$ +154° (*c* 0.173, H_2O, 24 h); FAB-MS, *m/z* 313 $[(M+H)^+]$, 335 $[(M+Na)^+]$; retention time in HPLC: 4.2 min [Cosmosil 5C18 AR, 4.6×250 mm; solvent: H_2O; flow rate: 1.0 ml min^{-1}; detection: RI (16×10^{-6} RIU) POL+]. ^1H and ^{13}C NMR of **1** are shown in Tables 1 and 2, respectively. Found: C, 39.54; H, 6.84%. Calcd for $C_{11}H_{20}O_{10}\cdot 1.2H_2O$: C, 39.57; H, 6.76%.

1-Propenyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (12a). *O*-Acetylation of compound **13a** (735 mg, 1.18 mmol) was carried out with Ac_2O (6 ml, 63 mmol) and pyridine (6 ml, 75 mmol) to give **12a** as an oily product: Yield 880 mg (99.5%); $[\alpha]_D^{24}$ +73.3° (*c* 0.360,

$CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ=1.57 (3H, dd, J=1.7, 6.9 Hz, OCH=CH-C$\underline{H}_3$), 1.81 (3H, s, Ac), 2.06 (3H, s, Ac), 2.09 (3H, s, Ac), 3.34 (1H, dd, J=3.2, 9.9 Hz, H_B-2), 3.4—4.4 (8H, m), 4.80 (1H, d, J=3.7 Hz, H_B-1), 4.55—4.9 (6H, m, C$\underline{H}_2C_6H_5$×3), 4.97 (1H, dd, J=3.7, 9.6 Hz, H_A-2), 5.12—5.26 (3H, m, H_A-1, H_A-4, OCH=C$\underline{H}$-CH_3), 6.14 (1H, m, J=1.7, 12.2 Hz, OC$\underline{H}$=CH-CH_3), 7.2—7.4 (15H, m, $CH_2C_6\underline{H}_5$×3). Found: C, 65.53; H, 6.46%. Calcd for $C_{41}H_{48}O_{13}$: C, 65.76; H, 6.46%.

***O*-(2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-2,4,6-tri-*O*-acetyl-D-glucopyranose (15).** 1-Propenyl group of compound **12a** (845 mg, 1.13 mmol) was removed with I_2 (574 mg, 2.26 mmol) in THF (39 ml) and water (6 ml) as described for the preparation of **14**. The crude product was purified by silica-gel column chromatography (20 g, 1.5×25 cm, benzene–AcOEt=3 : 1) to give a homogeneous oily product: Yield 760 mg (94.9%); $[\alpha]_D^{20}$ +48.1° (c 1.06, $CHCl_3$, 24 h). Found: C, 64.04; H, 6.12%. Calcd for $C_{38}H_{44}O_{13}\cdot 0.2H_2O$: C, 64.07; H, 6.28%.

***O*-(2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-2,4,6-tri-*O*-acetyl-α,β-D-glucopyranosyl Trichloroaceotimidate (16).** To a solution of **15** (713 mg, 1.01 mmol) in CH_2Cl_2 (8.5 ml) were added CCl_3CN (570 μl, 5.7 mmol) and Cs_2CO_3 (42 mg, 0.13 mmol). The mixture was stirred at room temperature for 2 h. AcOEt and brine were added to the mixture. The organic layer was separated and worked up as usual to give an oily product as a 2 : 1 mixture (860 mg, quant) of the α- and β-anomers; ^1H NMR (270 MHz, $CDCl_3$) δ=5.77 (0.33H, d, J=8.2 Hz, $H_A\beta$-1), 6.45 (0.67H, d, J=4.0 Hz, $H_A\alpha$-1), 8.66 (1H, s, NH). The oily product obtained was subjected to the following reaction without purification.

***N*-Benzyloxycarbonyl-*O*-(2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-gluopyranosyl)-(1→3)-L-serine Benzyl Ester (18).** To a mixture of **16** (1.01 mmol), Z-Ser-OBzl (**17**) (399 mg, 1.21 mmol), and molecular sieves AW-300 (1.8 g) in 1,2-dichloroethane (30 ml) was added $BF_3\cdot Et_2O$ (149 ml, 1.21 mmol) under N_2 atmosphere at −12 °C. The mixture was stirred at −12 °C for 2 h, and AcOEt and a saturated $NaHCO_3$ solution were added. The organic layer was separated and worked up as usual. The residue was purified by silica-gel column chromatography (40 g, 1.5×50 cm, benzene–AcOEt=15 : 2) to give an oily product: Yield 675 mg (65.5%); $[\alpha]_D^{20}$ +7.7° (c 1.02, $CHCl_3$). Found: C, 66.07; H, 6.10; N, 1.18%. Calcd for $C_{56}H_{61}O_{17}N$: C, 65.94; H, 6.03; N, 1.37%.

***O*-α-D-Xylopyranosyl-(1→3)-*O*-β-D-glucopyranosyl-(1→3)-L-serine (2).** Compound **18** (100 mg, 0.0980 mmol) was dissolved in THF (5 ml) and MeOH (1 ml) and hydrogenated with Pd-black (70 mg) at room temperature under 6.5 kg cm^{-2} of H_2 overnight. Then $Pd(OH)_2$ (100 mg), MeOH (4 ml), and water (1 ml) were added to the mixture, the hydrogenation was further carried out for 2 h under the same conditions. The catalyst was filtered off, and the filtrate was concentrated. To the solution of the residue in MeOH (5 ml) was added $NH_2NH_2\cdot H_2O$ (1 ml), the solution was allowed to stand at room temperature for 5 h, and then acetone (7 ml) was added under ice cooling. The mixture was concentrated, and the residue was lyophilized from water. The crude product was purified by HPLC (column: Cosmosil 5C18 AR, 20×250 mm; solvent: H_2O; flow rate: 8.0 ml min^{-1}; detection: UV at 210 nm), and lyophilyzed to give **2** as a powder: Yield 23.0 mg (58.8 %); $[\alpha]_D^{22}$ +79.9° (c 0.139, H_2O); FAB-MS, m/z 400 [(M+H)$^+$]; retention time in HPLC: 4.0 min [Cosmosil 5C18 AR, 4.6×250 mm; solvent: H_2O; flow rate: 1.0 ml min^{-1}; detection: UV at 210 nm, RI (16×10^{-6} RIU) POL+]. ^1H and ^{13}C NMR of **2** are shown in Table 1 and 2, respectively. Found: C, 38.71; H, 6.68; N, 2.93%. Calcd for $C_{14}H_{25}O_{12}N\cdot 2H_2O$: C, 38.62; H, 6.71; N, 3.22%.

Allyl 2,4-Di-*O*-benzyl-α-D-xylopyranoside (19a).[23] To a solution of allyl α-D-xylopyranoside (6.00g, 31.5 mmol) in DMSO (200 ml) was added 60% NaH (oil suspension, 3.15 g, 78.8 mmol) under ice cooling, and the mixture was stirred at room temperature for 30 min. Benzyl bromide (9.4 ml, 79 mmol) was added to the mixture under ice cooling. The mixture was stirred at room temperature overnight. AcOEt and brine were added to the mixture. The organic layer was separated, washed with water, and worked up as usual. The residue was purified by silica-gel column chromatography (160 g, 3×50 cm, benzene–AcOEt=30 : 1) to give an oily product: Yield 4.96 g (42.4 %); $[\alpha]_D^{26}$ +78.1° (c 0.790, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ=3.34 (1H, dd, J=3.5, 9.5 Hz, H-2), 3.50—3.65 (3H, m, H-4,5,5'), 3.92 (1H, m, OC$\underline{H}_2$CH=CH_2), 4.05 (1H, dd, J=8.2, 9.5 Hz, H-3), 4.13 (1H, m, OC$\underline{H}_2$CH=CH_2), 4.6—4.80 (6H, m, C$\underline{H}_2C_6H_5$×3), 4.74 (1H, d, J=3.5 Hz, H-1), 5.19 (1H, m, OCH_2CH=C$\underline{H}_2$), 5.31 (1H, m, OCH_2CH=C$\underline{H}_2$), 5.89 (1H, m, $OCH_2C\underline{H}$=CH_2), 7.2—7.4 (15H, m, $CH_2C_6\underline{H}_5$×3). Found: C, 70.35; H, 7.04%. Calcd for $C_{22}H_{26}O_5\cdot 0.3H_2O$: C, 70.31; H, 7.13%. A part of the product was *O*-acetylated with Ac_2O and pyridine to give allyl 3-*O*-acetyl-2,4-di-*O*-benzyl-α-D-xylopyranoside: ^1H NMR (270 MHz, $CDCl_3$) δ=2.00 (3H, s, Ac), 3.41 (1H, dd, J=3.6, 9.9 Hz, H-2), 3.52 (1H, m, H-4) , 3.60—3.65 (2H, m, H-5,5'), 3.95 (1H, m, OC$\underline{H}_2$CH=CH_2), 4.15 (1H, m, OC$\underline{H}_2$CH=CH_2), 4.49—4.60 (6H, m, C$\underline{H}_2C_6H_5$×3), 4.78 (1H, d, J=3.6 Hz, H-1), 5.19 (1H, m, OCH_2CH=C$\underline{H}_2$), 5.31 (1H, m, OCH_2CH=C$\underline{H}_2$), 5.47 (1H, dd, J=8.9, 9.9 Hz, H-3), 5.89 (1H, m, $OCH_2C\underline{H}$=CH_2), 7.2—7.4 (15H, m, $CH_2C_6\underline{H}_5$×3).

Allyl 2,4-Di-*O*-benzyl-β-D-xylopyranoside (19b).[23] Compound **19b** was prepared from allyl β-D-xylopyranoside (1.90 g, 10.0 mmol) using 60% NaH (880 mg, 22.0 mmol) and benzyl bromide (2.62 ml, 22.0 mmol) as described for the preparation of **19a**. The crude product was purified by silica-gel column chromatography (65 g, 2×42 cm, benzene–AcOEt=10 : 1) to give an oily product: Yield 720 mg (19.5 %); $[\alpha]_D^{26}$ −3.3° (c 0.850, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ=2.52 (1H, d, J=2.2 Hz, OH-3), 3.21 (1H, dd, J=9.7, 11.6 Hz, H-5ax), 3.26 (1H, dd, J=7.4, 9.0 Hz, H-2), 3.55 (1H, m, H-4), 3.67 (1H, ddd, J=2.2, 9.0, 9.0 Hz, H-3), 3.92 (1H, dd, J=5.1, 11.6 Hz, H-5ax), 4.14 (1H, m, OC$\underline{H}_2$CH=CH_2), 4.37 (1H, m, OC$\underline{H}_2$CH=CH_2), 4.39 (1H, d, J=7.4 Hz, H-1), 4.6—5.0 (6H, m, C$\underline{H}_2C_6H_5$×3), 5.23 (1H, m, OCH_2CH=C$\underline{H}_2$), 5.44 (1H, m, OCH_2CH=C$\underline{H}_2$), 5.96 (1H, m, $OCH_2C\underline{H}$=CH_2), 7.2—7.4 (15H, m, $CH_2C_6\underline{H}_5$×3). Found: C, 69.83; H, 7.05%. Calcd for $C_{22}H_{26}O_5\cdot 0.4H_2O$: C, 69.97; H, 7.15%.

Allyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-2,4-di-*O*-benzyl-α-D-xylopyranoside (20a) and Allyl *O*-(2,3,4-Tri-*O*-benzyl-β-D-xylopyranosyl)-(1→3)-2,4-di-*O*-benzyl-α-D-xylopyranoside (20b). The coupling reaction of **19a** (333 mg, 0.900 mmol) and 2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl fluoride (**10**) (422 mg, 1.00 mmol) was carried out using $SnCl_2$ (190 mg, 1.00 mmol), $AgClO_4$ (207 mg, 1.00 mmol), and powdered molecular sieves 4A (2 g) in ether (20 ml) as described for the preparation of **11a** and **11b**. The crude product was purified by silica-gel column chromatography (40 g, 1.5×50 cm, benzene–AcOEt=30 : 1) to give an oily product as a 1.7 : 1 mixture (590 mg, 84.9%) of the α- and β-anomers; ^1H NMR (270 MHz,

$CDCl_3$) δ=3.15 (0.37H, dd, J=9.7, 11.4 Hz, $H_C\beta$-5ax), 3.3—5.0 (m), 5.25 (2H, m, $OCH_2CH{=}C\underline{H}_2$), 5.59 (0.63H, d, J=3.7 Hz, $H_C\alpha$-1), 5.9 (1H, m, $OCH_2C\underline{H}{=}CH_2$), 7.2—7.4 (25H, m, $CH_2C_6\underline{H}_5\times5$).

1-Propenyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-2,4-di-*O*-benzyl-α-D-xylopyranoside (21a). The allyl group of the mixture of **20a** and **20b** (763 mg, 0.988 mmol) was isomerized to 1-propenyl group with $[Ir(COD)(PMe(C_6H_5)_2)_2]PF_6$ (30 mg, 0.035 mmol) in THF (20 ml) as described for the preparation of **12a** and **12b**. The crude product was purified by silica-gel column chromatography (70 g, 2×45 cm, benzene–AcOEt=40 : 1) to give **21a** and 1-propenyl *O*-(2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl)-(1→3)-2,4-di-*O*-benzyl-α-D-xylopyranoside (**21b**) as oily products.

21a: Yield 407 mg (53.3%); $[\alpha]_D^{26}$ +67.4° (*c* 1.05, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.53 (3H, dd, J=1.6, 6.9 Hz, $OCH{=}CH{-}C\underline{H}_3$), 3.4—3.6 (6H, m, H_B-2,5,5′, H_C-2,3,4), 3.72 (1H, m, H_B-4), 3.9—4.15 (2H, m, H_C-5,5′), 4.22 (1H, dd, J=9.2, 9.2 Hz, H_B-3), 4.88 (1H, d, J=3.5 Hz, H_B-1), 4.5—5.0 (10H, m, $C\underline{H}_2C_6H_5\times5$), 5.15 (1H, m, J=6.9, 13 Hz, $OCH{=}C\underline{H}{-}CH_3$), 5.59 (1H, d, J=3.7 Hz, H_C-1), 6.08 (1H, m, J=1.6, 13 Hz, $OC\underline{H}{=}CH{-}CH_3$), 7.2—7.4 (25H, m, $CH_2C_6\underline{H}_5\times5$); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=12.3 ($OCH{=}CH{-}\underline{C}H_3$), 59.8, 60.3 ($C_B$-5, C_C-5), 72.4, 72.8, 73.0, 73.4, 74.6, 75.4, 77.8, 78.7, 79.5, 79.6, 81.2 (C_B-2,3,4, C_C-2,3,4, $\underline{C}H_2C_6H_5\times5$), 96.2, 96.8 ($C_B$-1, C_C-1), 104.7 ($OCH{=}\underline{C}H{-}CH_3$), 127.1—128.5 (aromatic $\underline{C}H$), 137.8, 138.2, 138.3, 138.7, 139.1 (aromatic C×5), 143.0 ($O\underline{C}H{=}CH{-}CH_3$). Found: C, 74.31; H, 6.74%. Calcd for $C_{48}H_{52}O_9$: C, 74.59; H, 6.78%.

21b: Yield 230 mg (30.1 mg); $[\alpha]_D^{26}$ +55.8° (*c* 1.00, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.53 (3H, dd, J=1.7, 6. 9 Hz, $OCH{=}CH{-}C\underline{H}_3$), 3.16 (1H, dd, J=9.9, 11.6 Hz, H_C-5ax), 3.3—3.7 (6H, m, H_B-2,4,5,5′, H_C-2,3,4), 3.94 (1H, dd, J=4.8, 11.6 Hz, H_C-5eq), 4.27 (1H, dd, J=8.2, 9.4 Hz, H_B-3), 4.72 (1H, d, J=3.7 Hz, H_B-1), 4.95 (1H, d, J=7.7 Hz, H_C-1), 4.5—5.0 (6H, m, $C\underline{H}_2C_6H_5\times3$), 5.12 (1H, m, J=6.9, 13 Hz, $OCH{=}C\underline{H}{-}CH_3$), 6.01 (1H, m, J=1.6, 13 Hz, $OC\underline{H}{=}CH{-}CH_3$), 7.2—7.4 (15H, m, $CH_2C_6\underline{H}_5\times3$). Found: C, 74.37; H, 6.74%. Calcd for $C_{48}H_{52}O_9$: C, 74.59; H, 6.78%.

***O*-(2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-2,4-di-*O*-benzyl-D-xylopyranose (22).** 1-Propenyl group of compound **21a** (1.71 g, 2.21 mmol) was removed with I_2 (1.12 g, 4.42 mmol) in THF (50 ml) and water (16 ml) as described for the preparation of **14**. The crude product was purified by silica-gel column chromatography (70 g, 2×45 cm, benzene–AcOEt=6 : 1) to give an oily product: Yield 1.46 g (90.0%); $[\alpha]_D^{20}$ +43.6° (*c* 1.04, $CHCl_3$, 6h). Found: C, 72.38; H, 6.47%. Calcd for $C_{45}H_{48}O_9\cdot0.8H_2O$: C, 72.33; H, 6.69%.

***O*-(2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-2,4-di-*O*-benzyl-α,β-D-xylopyranosyl Fluoride (23).** To a solution of compound **22** (2.00 g, 2.73 mmol) in CH_2Cl_2 (30 ml) were added 2-fluoro-1-methylpyridinium *p*-toluenesulfonate (1.30 g, 5.46 mmol) and triethylamine (1.53 ml, 10.9 mmol). The solution was stirred at room temperature for 3 h. EtOAc and water were added to the solution. The organic layer was separated, washed with a saturated $NaHCO_3$ solution, and worked up as usual. The residue was purified by silica-gel column chromatography (70 g, 2×45 cm, benzene–AcOEt=30 : 1) to give an oily product as a 3.2 : 1 mixture (1.70 g, 85.0%) of the α- and β-anomers: ^{1}H NMR (270 MHz, $CDCl_3$) δ=5.26 (0.24H, d, J=3.5 Hz, $H_C\beta$-1), 5.37 (0.24H, dd, J=5.5, 53.5Hz, $H_B\beta$-1), 5.45 (0.76H, dd, J=2.7, 52.9 Hz, $H_B\alpha$-1), 5.59 (0.76H, d, J=3.7 Hz, $H_C\alpha$-1). Found: C, 73.53; H, 6.42%. Calcd for $C_{45}H_{47}O_8F$: C, 73.55; H, 6.45%.

Allyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-*O*-(2,4-di-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (24a). The coupling reaction of allyl 2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (**9a**) (793 mg, 2.29 mmol) and the fluoride **23** (1.60 g, 2.18 mmol) was carried out using $SnCl_2$ (455 mg, 2.40 mmol), $AgClO_4$ (498 mg, 2.40 mmol), and powdered molecular sieves 4A (5 g) in ether (60 ml) as described for the preparation of **11a** and **11b**. The crude product was purified by silica-gel column chromatography (70 g, 2×45 cm, benzene–AcOEt=10 : 1) to give **24a** and allyl *O*-(2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-*O*-(2,4-di-*O*-benzyl-β-D-xylopyranosyl)-(1→3)-2,4,6-tri-O-acetyl-α-D-glucopyranoside (**24b**) as oily products.

24a: Yield 1.67 g (72.3%); $[\alpha]_D^{20}$ +71.1° (*c* 1.10, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.71 (3H, s, Ac), 2.05 (3H, s, Ac), 2.10 (3H, s, Ac), 3.39 (1H, dd, J=3.2, 9.4 Hz, H_B-2), 3.43 (1H, dd, J=3.5, 9.1 Hz, H_C-2), 3.45—3.7 (5H, m, H_B-4,5,5′, H_C-3,4), 3.9—4.25 (9H, m, H_A-3,5,6,6′, H_B-3, H_C-5,5′, $OC\underline{H}_2CH{=}CH_2$), 4.5—4.8 (8H, m, $C\underline{H}_2C_6H_5\times4$), 4.81 (1H, d, J=3.2 Hz, H_B-1), 4.85—5.0 (4H, m, H_A-1,2, $C\underline{H}_2C_6H_5$), 5.19 (1H, dd, J=9.9, 10.1 Hz, H_A-4), 5.28 (2H, m, $OCH_2CH{=}C\underline{H}_2$), 5.58 (1H, d, J=3.5 H z, H_C-1), 5.80 (1H, m, $OCH_2C\underline{H}{=}CH_2$), 7.2—7.4 (25H, m, $CH_2C_6\underline{H}_5\times5$); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=20.5, 20.8, 20.9 ($CO\underline{C}H_3\times3$), 60.1, 60.4, 62.1 ($C_A$-6, C_B-5, C_C-5), 67.5, 68.55, 68.61, 72.2, 72.6, 73.2, 73.4, 74.0, 75.5, 77.2, 78.3, 78.6, 79.0, 79.3, 79.7, 81.1 (C_A-2,3,4,5, C_B-2,3,4, C_C-2,3,4, $O\underline{C}H_2CH{=}CH_2$, $\underline{C}H_2C_6H_5\times5$), 95.3, 96.4, 98.6 ($C_A$-1, C_B-1, C_C-1), 118.1 ($OCH_2CH{=}\underline{C}H_2$), 127.0—128.7 (aromatic $\underline{C}H$), 133.3 ($OCH_2CH{=}\underline{C}H_2$), 137.7, 138.1, 138.2, 138.7, 139.0 (aromatic C×5), 169.3, 170.2, 170.8 ($\underline{C}OCH_3\times3$). Found: C, 66.96; H, 6.35%. Calcd for $C_{60}H_{68}O_{17}\cdot0.7H_2O$: C, 67.11; H, 6.51%.

24b: Yield 347 mg (15.0%); $[\alpha]_D^{20}$ +83.4° (*c* 1.22, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.84 (3H, s, Ac), 2.00 (3H, s, Ac), 2.10 (3H, s, Ac) 3.14 (1H, dd, J=9.6, 11.4 Hz, H_B-5ax), 3.34 (1H, dd,J=7.3, 8.9 Hz, H_B-2), 3.42 (1H, dd, J=3.5, 9.6 Hz, H_C-2) , 3.45—3.58 (2H, m, H_C-5,5′), 3.67 (1H, m, H_B-4), 3.7—3.9 (10H, m, H_A-3,5,6,6′, H_B-3,5eq, H_C-3,4, $OC\underline{H}_2$-$CH{=}CH_2$), 4.51 (1H, d, J=7.3 Hz, H_B-1), 4.45—4.9 (11H, m, H_A-2, $C\underline{H}_2C_6H_5\times5$), 5.03 (1H, dd, J=9.7, 9.9 Hz, H_A-4), 5.15 (1H, d, J=3.7 Hz, H_A-1), 5.22 (2H, m, $OCH_2CH{=}C\underline{H}_2$), 5.53 (1H, d, J=3.5 Hz, H_C-1), 5.85 (1H, m, $OCH_2C\underline{H}{=}CH_2$), 7.2—7.4 (25H, m, $CH_2C_6\underline{H}_5\times5$); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=20.6, 20.8, 20.9($CO\underline{C}H_3\times3$), 60.3, 62.3, 63.2 ($C_A$-6, C_B-5, C_C-5), 67.6, 68.3, 68.8, 72.4, 73.1, 73.8, 74.6, 74.7, 75.6, 78.5, 79.3, 79.58, 79.64, 81.11 (C_A-2,3,4,5, C_B-2,3,4, C_C-2,3,4, $O\underline{C}H_2CH{=}CH_2$, $\underline{C}H_2C_6H_5\times5$) 94.8, 96.6, 104.0 ($C_A$-1, C_B-1, C_C-1), 118.2 ($OCH_2CH{=}\underline{C}H_2$), 127.2—128.5 (aromatic $\underline{C}H$), 133.2 ($OCH_2CH{=}\underline{C}H_2$), 138.0, 138.1, 138.3, 138.5, 138.9 (aromatic C×5), 169.4, 170.2, 170.7 ($\underline{C}OCH_3\times3$). Found: C, 67.40; H, 6.37%. Calcd for $C_{60}H_{68}O_{17}\cdot0.3H_2O$: C, 67.57; H, 6.48%.

1-Propenyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-*O*-(2,4-di-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranoside (25). The allyl group of **24a** (1.60 g, 1.51 mmol) was isomerized to 1-propenyl group with $[Ir(COD)(PMe(C_6H_5)_2)_2]PF_6$ (40 mg, 0.047 mmol) in THF (20 ml) as described for the preparation of **12a** and **12b**. The crude product was purified by silica-gel column chromatography (65 g, 2×42 cm, benzene–AcOEt=10 : 1) to give a homogeneous oily product: Yield 1.53 g (95.6%); $[\alpha]_D^{20}$ +70.5° (*c* 1.34, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.57 (3H, dd,

J=1.5, 6.7 Hz, OCH=CH-C$\underline{H}_3$), 1.71 (3H, s, Ac), 2.04 (3H, s, Ac), 2.09 (3H, s, Ac), 3.39 (1H, dd, J=3.0, 8.7 Hz, H_B-2), 3.42 (1H, dd, J=3.7, 9.7 Hz, H_C-2), 3.45—3.7 (5H, m, H_B-4,5,5′, H_C-3,4), 3.85—4.20 (7H, m, H_A-3,5,6,6′, H_B-3, H_C-5,5′), 4.5—4.75 (8H, m, C$\underline{H}_2C_6H_5$×4), 4.82 (1H, d, J=3.0 Hz, H_B-1), 4.93 (2H, s, C$\underline{H}_2C_6H_5$), 4.96 (1H, dd, J=3.8, 8.9 Hz, H_A-2), 5.14 (1H, d, J=3.8 Hz, H_A-1), 5.15—5.30 (2H, m, H_A-4, OCH=C$\underline{H}$-CH$_3$), 5.58 (1H, d, J=3.5 Hz, H_C-1), 6.14 (1H, m, J=1.5, 12.2 Hz, OC$\underline{H}$=CH-CH$_3$), 7.2—7.4 (25H, m, CH$_2$C$_6$H$_5$×5). Found: C, 67.48; H, 6.45%. Calcd for $C_{60}H_{68}O_{17}\cdot 0.3H_2O$: C, 67.57; H, 6.48%.

***O*-(2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-*O*-(2,4-di-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-D-glucopyranose (29).** Compound **25** (407 mg, 0.384 mmol) was treated first with 0.08 M MeONa solution (120 ml) and then with I_2 (195 mg, 0.768 mmol) in THF (9.3 ml) and water (2.3 ml) as described for the preparation of **13a**, and **14**, respectively. The crude product was purified by HPLC [column: Cosmosil 5C18, 16.7×250 mm; solvent: CH$_3$CN–H$_2$O, gradient: 70—100% (2% min^{-1}); flow rate: 8.0 ml min^{-1}; detection: UV at 240 nm] to give an oily product: Yield 302 mg (87.8%); $[\alpha]_D^{20}$ +79.2° (*c* 0.994, CHCl$_3$, 24 h). Found: C, 68.05; H, 6.60%. Calcd for $C_{51}H_{58}O_{14}\cdot 0.3H_2O$: C, 68.03; H, 6.56%.

***O*-α-D-Xylopyranosyl-(1→3)-*O*-α-D-xylopyranosyl-(1→3)-D-glucopyranose (3).** Compound **29** (283 mg, 0.316 mmol) was hydrogenated with Pd-black (300 mg) in MeOH (20 ml), water (5 ml), and acetic acid (20 ml) at room temperature under 6.5 kg cm^{-2} of H_2 for 2 d. The catalyst was filtered off, and the filtrate was concentrated. The residue was purified by HPLC (column: Cosmosil 5C18 AR, 20×250 mm; solvent: H_2O; flow rate: 8.0 ml min^{-1}) and lyophilyzed to give **3** as a powder: Yield 99.2 mg (70.9%); $[\alpha]_D^{20}$ +198° (*c* 0.149, H_2O, 24 h); FAB-MS, *m/z* 445 [(M+H)$^+$], 467 [(M+Na)$^+$]; retention time in HPLC: 6.9 min [Cosmosil 5C18 AR, 4.6×250 mm; solvent: H_2O; flow rate: 1.0 ml min^{-1}; detection: RI (16×10^{-6} RIU) POL+]. ^{1}H and ^{13}C NMR of **3** are shown in Tables 1 and 2, respectively. Found: C, 40.82; H, 6.53%. Calcd for $C_{16}H_{28}O_{14}\cdot 1.5H_2O$: C, 40.77; H, 6.63%.

***O*-(2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-*O*-(2,4-di-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-2,4,6-tri-*O*-acetyl-D-glucopyranose (26).** Compound **25** (1.09 g, 1.03 mmol) was treated with I_2 (523 mg, 2.06 mmol) in THF (40 ml) and water (6 ml) as described for the preparation of **14**. The crude product was purified by silica-gel column chromatography (20 g, 1.5×25 cm, benzene–AcOEt=4 : 1) to give a homogeneous oily product: Yield 984 mg (93.7%); $[\alpha]_D^{20}$ +46.7° (*c* 1.35, CHCl$_3$, 24 h). Found: C, 67.33; H, 6.37%. Calcd for $C_{57}H_{64}O_{17}$: C, 67.05; H, 6.32%.

***O*-(2,3,4-Tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-*O*-(2,4-di-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-2,4,6-tri-*O*-acetyl-α,β-D-glucopyranosyl Trichloroacetimidate (27).** Compound **27** was prepared from compound **26** (960 mg, 0.941 mmol) in CH_2Cl_2 (10 ml) using CCl_3CN (600 μl, 6.0 mmol) and Cs_2CO_3 (30 mg, 0.092 mmol) as described for the preparation of **16**. The oily product obtained (1.10 g, quant) was subjected to the following reaction without purification.

***N*-Benzyloxycarbonyl-*O*-(2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-*O*-(2,4-di-*O*-benzyl-α-D-xylopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→3)-L-serine Benzyl Ester (28).** The coupling reaction of **27** (0.941 mmol) and Z-Ser-OBzl (**17**) (363 mg, 1.10 mmol) was carried out using $BF_3\cdot Et_2O$ (136 μl, 1.10 mmol) and molecular sieves AW-300 (2.4 g) in 1,2-dichloroethane (20 ml) as described for the preparation of **18**. The crude product was purified by silica-gel column chromatography (40 g, 1.5×50 cm, benzene–AcOEt=15 : 2) to give an oily product: Yield 830 mg (66.2%); $[\alpha]_D^{24}$ +20° (*c* 0.255, CHCl$_3$). Found: C, 67.39; N, 6.15; N, 1.06%. Calcd for $C_{75}H_{81}O_{21}N$: C, 67.61; H, 6.13; N, 1.05%.

***O*-α-D-Xylopyranosyl-(1→3)-*O*-α-D-xylopyranosyl-(1→3)-*O*-β-D-glucopyranosyl-(1→3)-L-serine (4).** Compound **28** (94.0 mg, 0.0706 mmol) was dissolved in THF (5 ml) and MeOH (1 ml) and hydrogenated with Pd-black (70 mg) at room temperature under 6.0 kg cm^{-2} of H_2 overnight. After MeOH (4 ml), water (1 ml), and acetic acid (20 ml) were added to the mixture, the hydrogenation was further continued for 4.5 h. The catalyst was filtered off, and the filtrate was concentrated. The residue was treated with $NH_2NH_2\cdot H_2O$(1 ml) in MeOH (5 ml) as described for the preparation of **2**. The crude product was purified by HPLC (column: Cosmosil 5C18 AR, 20×250 mm; solvent: H_2O; flow rate: 8.0 ml min^{-1}; detection: UV at 210 nm) and lyophilyzed to give **4** as a powder: Yield 20.3 mg (54.1 %); $[\alpha]_D^{22}$ +134° (*c* 0.141, H_2O); FAB-MS, *m/z* 532 [(M+H)$^+$]; retention time in HPLC: 5.2 min [Cosmosil 5C18 AR, 4.6×250 mm; solvent: H_2O; flow rate: 1.0 ml min^{-1}, detection: UV at 210 nm, RI (16×10^{-6} RIU) POL+]. ^{1}H and ^{13}C NMR of **4** are shown in Table 1 and 2, respectively. Found: C, 39.94; H, 6.61; N, 2.40%. Calcd for $C_{19}H_{33}O_{16}N\cdot 2.2H_2O$: C, 39.96; H, 6.60; N, 2.45%.

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