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Carbohydrate Research 325 (2000) 83–92

CARBOHYDRATE RESEARCH

Synthesis of a model compound related to an anti-ulcer pectic polysaccharide

Michiko Maruyama [a], Tadahiro Takeda [a,*], Noriko Shimizu [a], Noriyasu Hada [a], Haruki Yamada [b]

[a] *Kyoritsu College of Pharmacy, Shibakoen 1-5-30, Minato-ku, Tokyo 105-8512, Japan*
[b] *Oriental Medicine Research Center of Kitasato Institute, 5-9-1 Shirokane, Minato-ku, Tokyo 108-8642, Japan*

Received 29 September 1999; accepted 22 November 1999

Abstract

A stereocontrolled synthesis of the model compound for an anti-ulcer active polysaccharide (Bupleuran 2IIc) is described. Glycosidation of the disaccharide acceptor, 2-*O*-acetyl-3-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-galactopyranosyl trichloroacetimidate, with the disaccharide receptor, allyl 3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-galactopyranoside, using silver triflate (AgOTf) as a promoter gave the desired tetrasaccharide derivative, which was transformed into the acidic tetrasaccharide, corresponding to a segment of the rhamnogalacturonan (Bupleuran 2IIc) polysaccharide, propyl α-L-Rha-(1→4)-α-D-GalA-(1→2)-α-L-Rha-(1→4)-β-D-GalA, via removal of the corresponding ether and ester protecting groups, followed by oxidation.

Keywords: Acidic tetrasaccharide; Anti-ulcer pectic polysaccharide; *Bupleurum falcatum*; Chemical synthesis

1. Introduction

Yamada et al. [1] have reported that during a study of the polysaccharide components of Chinese herbs, the potent anti-ulcer polysaccharide (Bupleuran 2IIc) against HCl–ethanol induced ulcerogenesis in mice was obtained from a hot-water extract of the roots of *Bupleurum falcatum* L. (Japanese name, Saiko), which has been used in Chinese and Japanese herbal medicine for the treatment of chronic hepatitis, nephrosis syndrome and autoimmune diseases [2]. Bupleuran 2IIc showed higher activity than using a clinical anti-ulcer drug, Sucralfate [3], at the same dose.

Bupleuran 2IIc has a molecular weight of 63,000 and contains 93.6% galacturonic acid, with small amounts of neutral sugars such as rhamnose, arabinose, galactose, glucose, mannose and xylose. It has been characterized as a pectin, consisting of 85.8% of a polygalacturonan region, which is made up of mainly α-(1→4)-linked galacturonic acid with small amounts of 2,4- and 3,4-di-*O*-substituted galacturonic acid, and an 8.6% ramified region. The ramified region contains several short, neutral carbohydrate chains and a β-(1→6)-galactan chain attached to position-4 of either the 2-linked rhamnosyl residue through 4-linked galacturonic acid, or a 2-linked rhamnose linked directly to the rhamnogalacturonan core. The structure of the pectic polysaccharide consists of 'ramified' (rhamnogalacturonan with neutral side chains,

* Corresponding author. Tel.: +81-3-54002696; fax: +81-3-54002556.
E-mail address: takeda-td@kyoritsu-ph.ac.jp (T. Takeda)

0008-6215/00/$ - see front matter
PII: S0008-6215(99)00315-8

PG-1) and Kdo-containing (1→4)-α-D-galacturonan regions (PG-2) [4]. The backbone of PG-1 is composed of an α-L-Rha-(1→4)-α-D-GalA-(1→2)-repeating unit. The repeating unit of PG-1 was the target for the synthetic studies as part of our investigations on the synthesis of oligosaccharides of biological interest.

The tetrasaccharide derivative, α-L-Rha-(1→4)-α-D-Gal-(1→2)-α-L-Rha-(1→4)-β-D-Gal (**20**) was obtained by condensation of allyl 3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (**11**) with 2-*O*-acetyl-3-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-galactopyranosyl trichloroacetimidate (**14**) in the presence of silver triflate (AgOTf) to give the tetrasaccharide derivative (**16**). Deacetylation of compound **16**, followed by debenzylation and oxidation, gave the dicarboxylic acid tetrasaccharide, propyl α-L-Rha-(1→4)-α-D-GalA-(1→2)-α-L-Rha-(1→4)-β-D-GalA (**21**).

2. Results and discussion

We now describe the synthesis of this repeating acidic tetrasaccharide, the propyl glycoside, α-L-Rha-(1→4)-α-D-GalA-(1→2)-α-L-Rha-(1→4)-β-D-GalA (**21**), as a model compound. In the course of its synthesis, it is difficult to synthesize a galacturonic acid with the 4-position free as a starting material, so we used D-galactose instead of the D-galacturonic acid. Synthesis of the neutral tetrasaccharide derivative (**16**) was carried out by the coupling of the allyl diglycoside acceptor (**11**), having the 4-position free, and the non-reducing end disaccharide imidate (**14**).

Allyl 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (**3**) was prepared in 97% yield by using allyl 2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (**1**) [5] as a galactosyl acceptor and the readily available 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl trichloroacetimidate (**2**) [6] as a rhamnosyl donor in the presence of AgOTf as a promotor in dichloromethane. The anomeric configuration of compound **3** was confirmed by ^{1}H NMR spectroscopy, the signals for H-1 and H-1′ being observed at δ 4.40 (J 7.9 Hz) and 5.20 (J 1.8 Hz), respectively. In the ^{13}C NMR spectrum (Table 1), the CH coupling of the signal of C-1 (99.0 ppm) was 178 Hz, as determined in an INEPT experiment, so the newly formed glycosidic bond is linked in the α configuration. A heteronuclear multiple bond correlation (HMBC) experiment showed a correlation between H-1′ (5.20 ppm) and the C-4 carbon (73.6 ppm). Removal of the acetyl groups of **3** with NaOMe in MeOH gave the disaccharide (**4**, 70%) with the 2′,3′,4′-positions free. Isopropylidenation of **4** with 2,2-dimethoxypropane in the presence of *p*-TsOH gave compound **5** (93%), which was selectively mono-*O*-(*p*-methoxybenzyl)ated and/or mono-*O*-benzylated with *p*-methoxybenzyl chloride and/or benzyl bromide in the presence of NaH in *N*,*N*-dimethylformamide to afford the compound **6** (65%) and/or **7** (82%). Compounds **6** and/or **7** were converted into the 3′-*O*-(*p*-methoxybenzyl)ated and/or 3′-*O*-benzylated disaccharide acceptor **10** or **11** by acid-catalyzed O-deisopropylidenation, followed by selective benzylation using *n*-Bu_2SnO, BnBr and *n*-Bu_4NBr in benzene [7]. These compounds were used partly as acceptors.

Meanwhile, compounds **10** and **11** were acetylated with acetic anhydride to give compounds **12** and **13**. Donors **14** and **15** were prepared from **12** and **13** by deallylation with palladium chloride in 90% acetic acid containing sodium acetate, followed by treatment of the resulting hemiacetal with trichloroacetonitrile and DBU in dichloromethane [8] (Scheme 1).

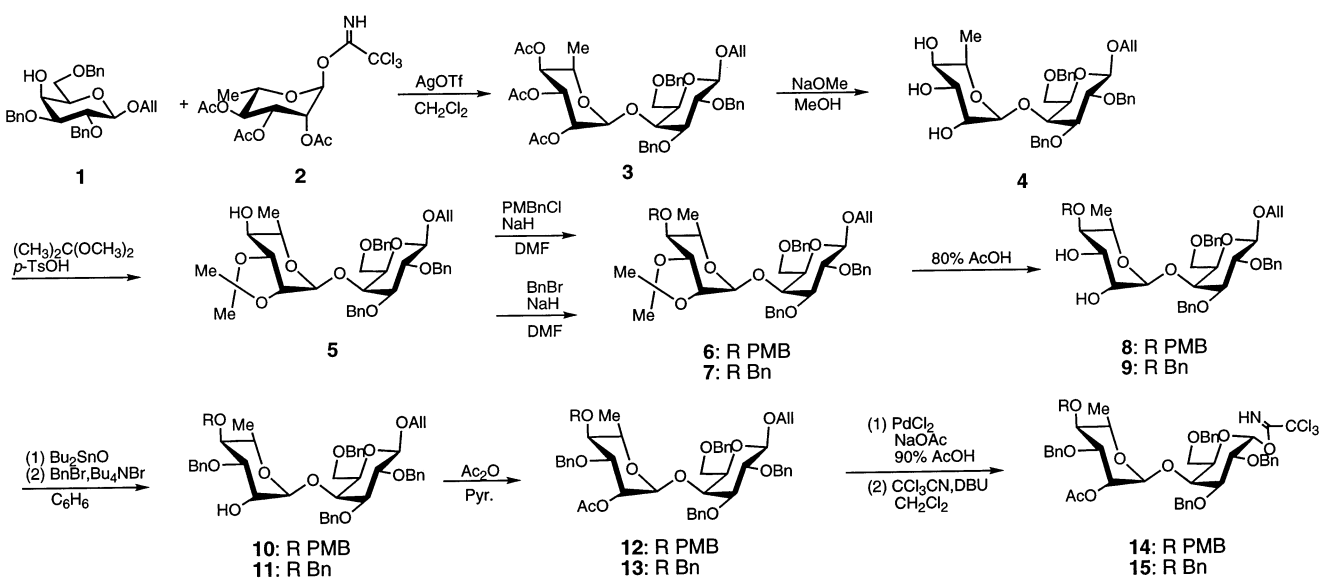
The coupling of **11** and **14** in the presence of AgOTf gave the expected product **16** (49% yield). Similarly, the reaction of **10** with the acceptor disaccharide **15** gave tetrasaccharide **17** (67% yield).

Recently, Reimer and co-workers have synthesized a hydroxyl-protected tetrasaccharide intermediate corresponding to a segment of the rhamnogalacturonan I polysaccharide, using the glycosyl trichloroacetimidate technique [9].

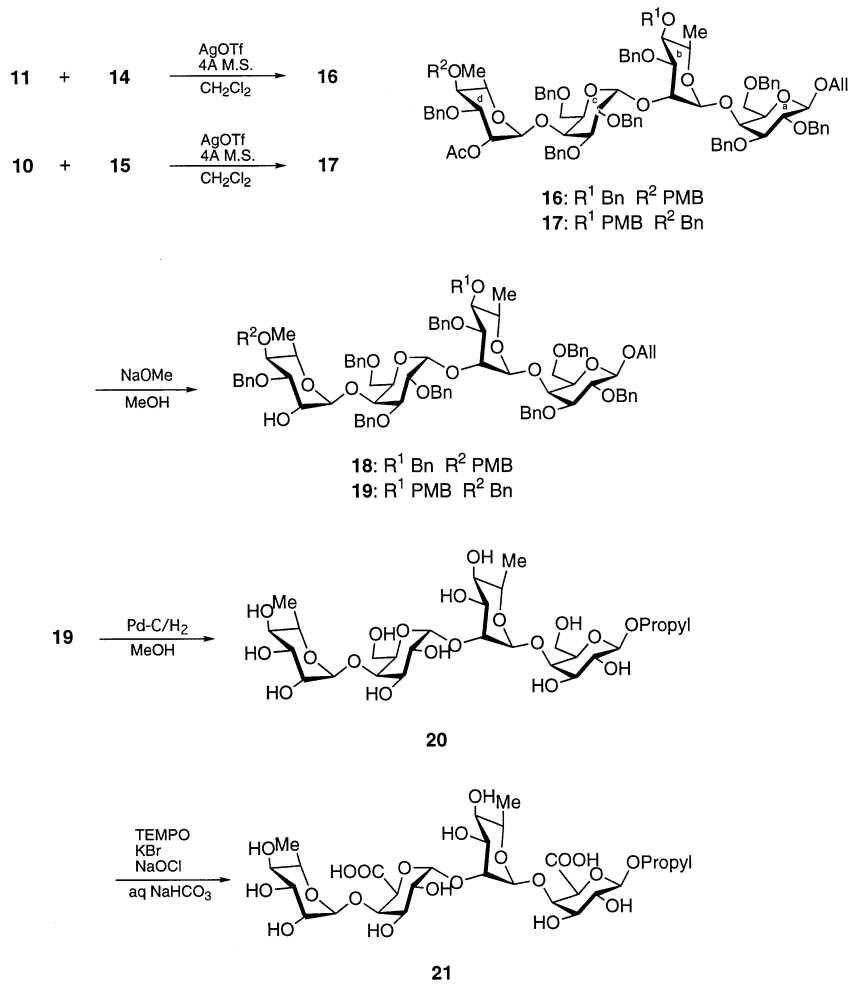
The structural assignment of these products was based on the comparison of their ^{1}H and ^{13}C NMR data. The presence of a characteris-

Table 1
^{13}C NMR data (δ) for compounds **3**–**12**

Carbon atom	Compound									
	3	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
C-1	103.0	103.0	103.0	103.0	103.0	102.9	103.0	102.9	103.0	103.0
C-2	79.3	79.2	79.1	79.1	79.0	79.2	79.2	79.1	79.2	79.0
C-3	81.4	81.8	81.7	81.8	81.8	81.8	81.8	81.7	81.8	81.5
C-4	73.6	71.8	71.7	71.3	71.3	72.4	72.3	72.4	72.5	72.4
C-5	72.9	73.5	73.4	73.5	71.3	71.2	73.2	73.5	73.4	73.1
C-6	69.0	69.1	69.3	69.3	69.3	69.1	69.1	69.1	69.2	67.0
C-1′	99.0	100.9	98.1	97.9	97.9	100.6	100.7	100.5	100.5	99.1
($J_{C\text{-}1',\ H\text{-}1'}$)	(178 Hz)									
C-2′	69.8	71.0	76.0	76.2	76.2	71.1	71.1	68.6	69.7	68.9
C-3′	69.2	71.5	78.3	78.4	78.3	71.2	71.2	79.5	79.7	78.0
C-4′	71.1	72.9	74.6	80.6	80.9	81.1	81.5	79.7	79.9	79.5
C-5′	67.0	69.0	66.1	65.2	65.2	68.0	68.0	68.1	68.1	68.4
C-6′	17.5	17.7	17.2	17.8	17.8	18.1	18.1	18.0	18.0	18.1
–CH=	134.0	133.8	134.0	134.0	134.0	134.0	134.0	134.0	134.1	134.0
CH_2 (All)	70.5	70.6	70.5	70.5	70.4	70.4	70.4	70.3	70.5	70.4
CH_2Ph	75.5	75.3	75.1	75.2	75.1	75.3	75.3	75.1	75.2	75.1
	73.6	73.4	73.6	73.6	73.5	74.3	74.6	74.7	75.1	74.9
	73.3	73.0	73.0	73.0	73.0	73.6	73.6	73.3	73.6	73.5
	72.9	73.3	72.7	72.7		73.3		73.1	73.2	73.2
								72.0	72.1	71.7
CH_3(Ac)	20.89									21.1
	20.84									
	20.76									
C=O(Ac)	170.1									169.8
	169.8									
	169.6									
$C(CH_3)_2$			109.1	108.8	108.8					
$C(CH_3)$			28.1	28.1	28.0					
			26.3	26.4	26.4					
CH_3O				55.3		55.3		55.1		55.3



Scheme 1.



Scheme 2.

tic signal for *p*-methoxybenzyl and one acetyl group in the ^{1}H NMR spectra of **16** and **17** demonstrated that they resembled tetrasaccharide derivatives. The ^{13}C NMR spectrum of **16** contained signals for anomeric carbons at 103.0 (157 Hz, C-1a), 99.0 (174 Hz, C-1d), 97.9 (170 Hz, C-1b), and 95.5 ppm (168 Hz, C-1c), which indicated the newly formed glycosidic linkage at C-1c to be of the α configuration.

Deacetylation of **16** with methanolic sodium methoxide gave **18** (93%). Debenzylation with Pd–C then gave the propyl tetrasaccharide compound **20**. During the deallylation of the allyl glycoside **18**, oxidation of the allyl to the 2-oxopropyl group was encountered. Oxidation of **20** to the uronic acid **21** was carried out with 2,2,6,6-tetramethylpiperidine 1-oxide (TEMPO), KBr and NaOCl in aqueous sodium hydrogencarbonate (50%) [10] (Scheme 2). The structure and purity of **21** were established by ^{1}H, ^{13}C NMR spectroscopy and MALDI-TOFMS spectrometry.

3. Experimental

General.—Optical rotations were determined with a Jasco DIP-140 digital polarimeter. ^{1}H and ^{13}C NMR spectra were recorded with a Jeol JNM A500 FT NMR spectrometer. Tetramethylsilane was the internal standard for solutions in $CDCl_3$ and/or CD_3OD, and sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DDS) for solutions in D_2O. TOF-MAS was recorded on a perceptive voyager RP mass spectrometer. Thin-layer chromatography (TLC) was performed on Silica Gel 60 F_{254} (E. Merck) with detection by quenching of UV fluorescence (254 nm) and by spraying with a 10% H_2SO_4 solution. Column chromatography was carried out on Silica Gel 60

(E. Merck) or IATROBEADS 6RS-8060. High-performance liquid chromatography (HPLC) was carried out using a Shimadzu SCL-10 A with a Shimadzu SPD-10 A detector. HPLC conditions: column, CAPCELL PAK C_{18}: UG80A 5 μm; solvent, H_2O, 9 mL/min; detector, UV (210 nm). Allyl 2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (**1**) and 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl trichloroacetimidate (**2**) were prepared by literature methods [5,6].

Allyl 2,3,4-tri-O-*acetyl-α-L-rhamnopyranosyl-(1→4)-2,3, 6-tri*-O-*benzyl-β-D-galactopyranoside* (**3**).—A mixture of allyl 2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (**1**) (1.08 g, 2.2 mmol), 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl trichloroacetimidate (**2**, 1.80 g, 4.4 mmol), and 4 Å MS (400 mg) in dry CH_2Cl_2 (22 mL) was stirred for 1 h under argon and then at room temperature (rt) in the dark. Silver triflate (87.8 mg, 0.36 mmol) was added to the mixture. After 24 h $CHCl_3$ was added, the mixture was filtered through a pad of Celite, diluted with $CHCl_3$, and successively washed with water and satd aq $NaHCO_3$, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography using 50:1 benzene–acetone as eluent to provide **3** (1.63 g, 97%); R_f 0.64 (8:1 benzene–acetone); $[\alpha]_D^{22}$ −26.2° (*c* 4, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 7.37–7.25 (m, 15 H, aromatic), 5.98–5.92 (m, 1 H, –*CH*=CH_2), 5.50 (dd, 1 H, $J_{2',3'}$ 3.1 Hz, H-2′), 5.35 (dd, 1 H, $J_{3',4'}$ 9.8 Hz, H-3′), 5.34–5.20 (m, 2 H, CH_2=), 5.20 (d, 1 H, $J_{1',2'}$ 1.8 Hz, H-1′), 5.03 (t, 1 H, $J_{4',5'}$ 9.8 Hz, H-4′), 4.95–4.52 (m, 6 H, 3 × –CH_2Ph), 4.40 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.44–4.15 (m, 2 H, –CH_2CH=CH_2), 4.09 (bd, 1 H, H-4), 4.00 (m, 1 H, $J_{5',6'}$ 6.1 Hz, H-5′), 3.79 (dd, 1 H, $J_{2,3}$ 9.8 Hz, H-2), 3.72 (dd, 1 H, J_{gem} 9.2 Hz, H-6a), 3.67 (dd, 1 H, H-6b), 3.59 (t, 1 H, $J_{5,6}$ 6.4 Hz, H-5), 3.49 (dd, 1 H, $J_{3,4}$ 2.4 Hz, H-3), 2.04, 2.04, 1.97 (each s, 9 H, 3 × –CH_3), 1.14 (d, 3 H, H-6′). Anal. Calcd for $C_{42}H_{50}O_{13}$: C, 66.13; H, 6.61. Found: C, 66.02; H, 6.58.

Allyl α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-O-*benzyl-β-D-galactopyranoside* (**4**).—To a solution of compound **3** (10.3 g, 13.5 mmol) in MeOH (108 mL) was added NaOMe (215 mg). The mixture was stirred at rt for 24 h, then neutralized with Amberlite IR-120B (H^+), filtered, and concentrated. The residue was chromatographed on silica gel using 50:1 $CHCl_3$–MeOH as eluent to give **4** (6.02 g, 70%); R_f 0.36 (10:1 $CHCl_3$–MeOH), $[\alpha]_D^{23}$ −1.94° (*c* 2.4, $CHCl_3$); ^{1}H NMR data (CD_3OD): δ 7.36–7.22 (m, 15 H, aromatic), 5.97–5.91 (m, 1 H, –*CH*=CH_2), 5.34–5.15 (m, 2 H, CH_2=), 5.28 (d, 1 H, $J_{1',2'}$ 1.8 Hz, H-1′), 4.85–4.43 (m, 6 H, 3 × –CH_2Ph), 4.43 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 4.38–4.12 (m, 2 H, –CH_2-CH=CH_2), 4.15 (bd, 1 H, $J_{4,5}$ 2.4 Hz, H-4), 3.99 (dd, 1 H, $J_{2',3'}$ 3.7 Hz, H-2′), 3.73 (dd, 1 H, $J_{3',4'}$ 9.8 Hz, H-3′), 3.69 (m, 1 H, $J_{5',6'}$ 6.1 Hz, H-5′), 3.66 (m, 2 H, H-6), 3.65 (m, 1 H, $J_{5,6}$ 6.1 Hz, H-5), 3.61 (dd, 1 H, $J_{2,3}$ 9.8 Hz, H-2), 3.41 (t, 1 H, $J_{4',5'}$ 9.2 Hz, H-4′), 1.21 (d, 3 H, H-6′) Anal. Calcd for $C_{36}H_{44}O_{10}$: C, 67.91; H, 6.96. Found: C, 67.78; H, 6.88.

Allyl 2,3-O-*isopropylidene-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri*-O-*benzyl-β-D-galactopyranoside* (**5**).—To a solution of compound **4** (3.91 g, 6.1 mmol) in 2,2-dimethoxypropane (70 mL) was added *p*-TsOH (103 mg). The mixture was stirred at rt for 24 h, then neutralized with triethylamine and evaporated to give **5** (3.85 g, 93%); R_f 0.79 (10:1 $CHCl_3$–MeOH); $[\alpha]_D^{20}$ −1.06 (*c* 4.8 $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 7.34–7.24 (m, 15 H, aromatic), 5.99–15.92 (m, 1 H, –*CH*=CH_2), 5.58 (bs, 1 H, H-1′), 5.27 (dd, 2 H, CH_2=), 4.92–4.52 (m, 6 H, 3 × –CH_2Ph), 4.42 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 4.30 (bd, 1 H, $J_{2',3'}$ 6 1 Hz, H-2′), 4.16 (d, 1 H, $J_{4,5}$ 2.4 Hz, H-4), 4.46–4.12 (m, 2 H, –CH_2CH=CH_2), 4.05 (t, 1 H, $J_{3',4'}$ 6.7 Hz, H-3′), 3.72 (dd, 1 H, $J_{2,3}$ 2.4 Hz, H-4), 3.66 (m, 2 H, H-6), 3.66 (m, 1 H, $J_{5',6'}$ 6.1 Hz, H-5′), 3.58 (t, 1 H, $J_{5,6}$ 5.8 Hz, H-5), 3.50 (dd, 1 H, $J_{3,4}$ 2.4 Hz, H-3), 3.36 (m, 1 H, H-4′), 2.54 (d, 1 H, OH), 1.52, 1.32 (each s, 6 H, 2 × –CH_3), 1.21 (d, 3 H, H-6′). Anal. Calcd for $C_{39}H_{48}O_{10}$: C, 69.21; H, 7.15. Found: C, 69.08; H, 7.09.

Allyl 2,3-O-*isopropylidene-4*-O-*(p-methoxybenzyl)-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri*-O-*benzyl-β-D-galactopyranoside* (**6**).—To a solution of **5** (6.40 g, 9.46 mmol) in DMF (98 mL) was added NaH (1.58 g, 50% in mineral oil). The mixture was stirred for 1 h and then cooled to 0 °C, and *p*-methoxybenzyl chloride (1.96 mL) was added dropwise. The mixture was left at rt under vacuum for 1 h, then at

atmospheric pressure overnight. Excess NaH was destroyed by addition of MeOH. The mixture was partitioned between $CHCl_3$ and water, the aq phase was extracted with $CHCl_3$, and the combined organic phases were washed with water, dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed on silica gel using 10:1 hexane–EtOAc as eluent to provide **6** (4.69 g, 65%); R_f 0.68 (8:1 benzene–acetone); ^{1}H NMR data ($CDCl_3$): δ 7.36–7.26 (m, 19 H, aromatic), 5.95 (m, 1 H, $-CH$=CH_2), 5.60 (bs, 1 H, H-1′), 5.35–5.18 (m, 2 H, =CH_2), 4.92–4.49 (m, 8 H, 4 × $-CH_2$Ph), 4.40 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.46–4.10 (m, 2 H, $-CH_2$CH=CH_2), 4.29 (d, 1 H, $J_{2',3'}$ 7.3 Hz, H-2′), 4.24 (t, 1 H, $J_{3',4'}$ 9.8 Hz, H-3′), 4.15 (bd, 1 H, $J_{4,5}$ 1.4 Hz, H-4), 3.79 (m, 1 H, $J_{5',6'}$ 6.1 Hz, H-5′), 3.74 (dd, 1 H, $J_{2,3}$ 9.8 Hz, H-2), 3.64 (dd, 2 H, H-6), 3.56 (t, 1 H, $J_{5,6}$ 6.1 Hz, H-5), 3.51 (dd, 1 H, $J_{3,4}$ 3.1 Hz, H-3), 3.18 (dd, 1 H, $J_{4',5'}$ 7.3 Hz, H-4′), 3.81 (s, 3 H, OCH_3), 1.50, 1.33 (each s, 6 H, 2 × $-CH_3$), 1.18 (d, 3 H, H-6′). Anal. Calcd for $C_{47}H_{56}O_{11}$: C, 70.83; H, 7.08. Found: C, 70.69; H, 6.93.

*Allyl 4-*O*-benzyl-2,3-*O*-isopropylidene-α-*L*-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-*D*-galactopyranoside* (**7**).—To a solution of **5** (3.21 g, 4.74 mmol) in DMF (54 mL) was added NaH (790 mg, 50% in mineral oil). The mixture was stirred for 30 min and then cooled to 0 °C, and benzyl bromide (1.07 mL) was added dropwise. The mixture was left at rt under vacuum for 1 h, then at atmospheric pressure overnight. Excess NaH was destroyed by addition of MeOH. The mixture was partitioned between $CHCl_3$ and water, the aq phase was extracted with $CHCl_3$, and the combined organic phases were washed with water, dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed on silica gel using 10:1 hexane–EtOAc as eluent to provide **7** (3.00 g, 82%); R_f 0.77 (8:1 benzene–acetone); ^{1}H NMR data ($CDCl_3$): δ 7.37–7.21 (m, 20 H, aromatic), 5.99–5.91 (m, 1 H, $-CH$=CH_2), 5.60 (bs, 1 H, H-1′), 5.35–5.17 (m, 2 H, CH_2=), 4.93–4.50 (m, 8 H, 4 × $-CH_2$Ph), 4.41 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.45–4.08 (m, 2 H, $-CH_2$CH=CH_2), 4.30 (bd, 1 H, $J_{2',3'}$ 5.5 Hz, H-2′), 4.26 (t, 1 H, $J_{3',4'}$ 6.4 Hz, H-3′), 4.16 (d, 1 H, $J_{4,5}$ 3.1 Hz, H-4), 3.74 (dd, 1 H, $J_{2,3}$ 7.9 Hz, H-2), 3.72 (t, 2 H, H-6), 3.68 (dd, 1 H, $J_{5',6'}$ 6.1 Hz, H-5′), 3.57 (t, 1 H, $J_{5,6}$ 5.8 Hz, H-5), 3.50 (dd, 1 H, $J_{3,4}$ 2.4 Hz, H-3), 3.21 (dd, 1 H, $J_{4',5'}$ 7.3 Hz, H-4′), 1.49, 1.34 (each s, 6 H, 2 × $-CH_3$), 1.20 (d, 3 H, H-6′). Anal. Calcd for $C_{46}H_{54}O_{10}$: C, 72.04; H, 7.10. Found: C, 71.08; H, 7.03.

*Allyl 4-*O*-(*p*-methoxybenzyl)-α-*L*-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-*D*-galactopyranoside* (**8**).—A solution of compound **6** (4.69 g, 6.12 mmol) in 80% aq AcOH was stirred for 2.5 h at 50 °C. The resultant solution was concentrated and chromatographed on silica gel with 50:1 $CHCl_3$–MeOH as eluent to provide **8** (3.19 g, 67%); R_f 0.27 (8:1 benzene–acetone); ^{1}H NMR data ($CDCl_3$): δ 7.35–7.24 (m, 19 H, aromatic), 5.94 (m, 1 H, $-CH$=CH_2), 5.24 (d, 1 H, $J_{1',2'}$ 1.8 Hz, H-1′), 4.91–4.49 (m, 8 H, 4 × $-CH_2$Ph), 4.39 (d, 1 H, $J_{1',2'}$ 7.3 Hz, H-1), 4.42–4.12 (m, 2 H, $-CH_2$CH=CH_2), 4.10 (d, 1 H, $J_{4,5}$ 3.1 Hz, H-4), 4.04 (d, 1 H, $J_{2',3'}$ 3.7 Hz, H-2′), 3.94 (dd, 1 H, $J_{3',4'}$ 8.6 Hz, H-3′), 3.79 (m, 1 H, $J_{5',6'}$ 6.1 Hz, H-5′), 3.77 (s, 3 H, OCH_3), 3.69 (dd, 1 H, $J_{2,3}$ 9.8 Hz, H-2), 3.67 (m, 2 H, H-6), 3.55 (t, 1 H, $J_{5,6}$ 6.1 Hz, H-5), 3.48 (dd, 1 H, $J_{3,4}$ 2.4 Hz, H-3), 3.31 (t, 1 H, $J_{4',5'}$ 8.9 Hz, H-4′), 2.45, 2.38 (each d, 2 H, 2 × OH), 1.24 (d, 3 H, H-6′). Anal. Calcd for $C_{44}H_{52}O_{11}$: C, 70.58; H, 5.92. Found: C, 69.28; H, 5.81.

*Allyl 4-*O*-benzyl-α-*L*-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-*D*-galactopyranoside* (**9**).—A solution of compound **7** (3.00 g, 3.91 mmol) in 80% aq AcOH was stirred for 2.5 h at 50 °C. The resultant solution was concentrated to dryness, and the residue was chromatographed on silica gel using 50:1 $CHCl_3$–MeOH as eluent to provide **9** (2.67 g, 94%); R_f 0.17 (8:1 benzene–acetone); ^{1}H NMR data ($CDCl_3$): δ 7.34–7.21 (m, 20 H, aromatic), 5.98–5.90 (m, 1 H, $-CH$=CH_2), 5.34–5.17 (m, 2 H, CH_2=), 5.25 (d, 1 H, $J_{1',2'}$ 1.8 Hz, H-1′), 4.91–4.49 (m, 8 H, 4 × $-CH_2$Ph), 4.46–4.13 (m, 2 H, $-CH_2$CH=CH_2), 4.39 (d, 1 H, $J_{1,2}$ 7 9 Hz, H-1), 4.10 (d, 1 H, $J_{4,5}$ 3.1 Hz, H-4), 4.04 (bd, 1 H, H-2′), 3.97 (m, 1 H, H-3′), 3.80 (dd, 1 H, $J_{5',6'}$ 6.4 Hz, H-5′), 3.68 (dd, 1 H, $J_{2,3}$ 8.9 Hz, H-2), 3.63 (d, 2 H, H-6), 3.56 (t, 1 H, $J_{5,6}$ 6.1 Hz, H-5), 3.48 (dd, 1 H, $J_{3,4}$ 3.1 Hz, H-3), 3.34 (t, 1 H, $J_{4',5'}$ 9.2 Hz, H-4′), 2.45 (each d, 2 H, 2 × OH), 1.25 (d, 3 H, H-6′). Anal. Calcd for $C_{43}H_{50}O_{10}$: C, 71.06; H, 6.93. Found: C, 69.93; H, 6.81.

Allyl 3-O-benzyl-4-O-(p-methoxybenzyl)-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (**10**).—A mixture of compound **8** (3.19 g, 4.20 mmol), dibutyltin oxide (1.3 g), and dry benzene (52 mL) was stirred under reflux, using a calcium chloride drying tube, for 5 h. Benzene (26 mL) was distilled off, and the solution was cooled to 50 °C and treated with tetrabutylammonium bromide (1.5 g) and benzyl bromide (0.62 mL). After the mixture was stirred for 3 h at 50 °C, the solution was concentrated. The residue was stirred with EtOAc (52 mL) at 0 °C for 12 h. The solids were removed by filtration and the filtrate was concentrated. Purification of the residue by chromatography with 70:1 benzene–acetone as eluent provided **10** (3.30 g, 93%); R_f 0.51 (8:1 benzene–acetone); ^{1}H NMR data ($CDCl_3$): δ 7.36–7.12 (m, 24 H, aromatic), 5.95 (m, 1 H, $-CH$=CH_2), 5.34 (bs, 1 H, H-1′), 5.40–5.12 (m, 2 H, CH_2=), 4.97–4.47 (m, 10 H, 5 × $-CH_2$Ph), 4.40 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 4.43–4.03 (m, 2 H, $-CH_2$CH=CH_2), 4.18 (bd, 1 H, $J_{2',3'}$ 3.1 Hz, H-2′), 4.09 (bs, 1 H, H-4), 3.96 (dd, 1 H, $J_{3',4'}$ 9.2 Hz, H-3′), 3.83–3.78 (m, 1 H, $J_{5',6'}$ 6.1 Hz, H-5′), 3.72 (s, 3 H, OCH_3), 3.70–3.67 (m, 2 H, H-6), 3.64 (dd, 1 H, $J_{2,3}$ 9.2 Hz, H-2), 3.55 (t, 1 H, $J_{5,6}$ 6.7 Hz, H-5), 3.46 (t, 1 H, $J_{4',5'}$ 9.2 Hz, H-4′), 3.46 (t, 1 H, $J_{3,4}$ 9.2 Hz, H-3), 2.54 (d, 1 H, OH), 1.23 (d, 3 H, H-6′). Anal. Calcd for $C_{51}H_{58}O_{11}$: C, 72.32; H, 6.90. Found: C, 72.46; H, 6.78.

Allyl 3,4-di-O-benzyl-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (**11**).—A mixture of compound **9** (2.57 g, 3.54 mmol), dibutyltin oxide (1.1 g), and dry benzene (17.2 mL) was stirred under reflux, using calcium chloride drying tube, for 5 h. Benzene (8 mL) was distilled off, and the solution was cooled to 50 °C and treated with tetrabutylammonium bromide (1.26 g) and benzyl bromide (0.55 mL). After the mixture was stirred for 3 h at 50 °C, the solution was concentrated. The residue was stirred with EtOAc (52 mL) at 0 °C for 12 h. The solids were removed by filtration and the filtrate was concentrated. Purification of the residue by chromatography with 70:1 benzene–acetone as eluent provided **11** (2.62 g, 91%); R_f 0.49 (8:1 benzene–acetone); ^{1}H NMR data ($CDCl_3$): δ 7.37–7.24 (m, 25 H, aromatic), 6.00–5.92 (m, 1 H, $-CH$=CH_2), 5.34 (bs, 1 H, H-1′), 5.22–5.20 (m, 2 H, CH_2=), 4.91–4.49 (m, 10 H, 5 × $-CH_2$Ph), 4.44–4.13 (m, 2 H, $-CH_2$CH=CH_2), 4.39 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.19 (dd, 1 H, $J_{2',3'}$ 1.5 Hz, H-2′), 4.11 (d, 1 H, $J_{4,5}$ 3.1 Hz, H-4), 3.88 (dd, 1 H, $J_{3',4'}$ 3.3 Hz, H-3′), 3.81 (dd, 1 H, $J_{5',6'}$ 7.9 Hz, H-5′), 3.71–3.63 (m, 2 H, H-6), 3.64 (d, 1 H, $J_{2,3}$ 2.5 Hz, H-2), 3.56 (t, 1 H, $J_{5,6}$ 6.1 Hz, H-5), 3.49 (dd, 1 H, $J_{3,4}$ 3.1 Hz, H-3), 3.45 (t, 1 H, $J_{4',5'}$ 9.2 Hz, H-4′), 2.40 (s, 1 H, OH), 1.23 (d, 3 H, H-6′). Anal. Calcd for $C_{50}H_{56}O_{10}$: C, 73.51; H, 6.91. Found: C, 72.92; H, 6.82.

Allyl 2-O-acetyl-3-O-benzyl-4-O-(p-methoxybenzyl)-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (**12**).—To a solution of compound **10** (628 mg, 0.47 mmol) in pyridine (10 mL) was added Ac_2O (10 mL) at 0 °C over a period of 2 h. The resultant solution was poured into ice-water and extracted with $CHCl_3$. The organic phase washed with water, 5% HCl, and satd aq $NaHCO_3$, dried over Na_2SO_4, filtered and concentrated.

The residue was purified by column chromatography using 100:1 benzene–acetone as eluent to provide **12** (466 mg, 71%); R_f 0.70 (8:1 benzene–acetone); ^{1}H NMR data ($CDCl_3$): δ 7.37–6.84 (m, 24 H, aromatic), 5.99–5.91 (m, 1 H, $-CH$=CH_2), 5.59 (dd, 1 H, $J_{2',3'}$ 3.1 Hz, H-2′), 5.36–5.18 (m, 1 H, CH_2=), 5.23 (d, 1 H, $J_{1',2'}$ 1.8 Hz, H-1′), 4.93–4.45 (m, 10 H, 5 × $-CH_2$Ph), 4.43–4.11 (m, 2 H, $-CH_2$CH=CH_2), 4.10 (bd, 1 H, H-4), 3.94 (dd, 1 H, $J_{3',4'}$ 9.2 Hz, H-3′), 3.83 (m, 1 H, $J_{5',6'}$ 6.1 Hz, H-5′), 3.79 (s, 3 H, OCH_3), 3.70 (dd, 1 H, $J_{2,3}$ 9.8 Hz, H-2), 3.65 (m, 2 H, H-6), 3.55 (t, 1 H, $J_{5,6}$ 6.4 Hz, H-5), 3.48 (dd, 1 H, $J_{3,4}$ 3.1 Hz, H-3), 3.37 (t, 1 H, $J_{4',5'}$ 9.8 Hz, H-4′), 2.06 (s, 3 H, CH_3), 1.23 (d, 3 H, H-6). Anal. Calcd for $C_{53}H_{60}O_{12}$: C, 71.60; H, 6.80. Found: C, 70.92; H 6.68.

Allyl 2-O-acetyl-3,4-di-O-benzyl-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (**13**).—To a solution of compound **11** (2.62 g, 3.21 mmol) in pyridine (10 mL) was added Ac_2O (10 mL) at 0 °C for 12 h. The resultant solution was poured into ice-water and extracted with $CHCl_3$. The organic phase washed with water, 5% HCl and

satd aq $NaHCO_3$, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography using 100:1 benzene–acetone as eluent to provide **13** (2.73 g, 99%); R_f 0.71 (8:1 benzene–acetone); ^1H NMR data ($CDCl_3$): δ 7.37–7.20 (m, 25 H, aromatic), 5.99–5.92 (m, 1 H, $-CH{=}CH_2$), 5.60 (dd, 1 H, $J_{2',3'}$ 9.8 Hz, H-2′), 5.60–5.24 (m, 2 H, $=CH_2$), 5.32 (d, 1 H, $J_{1',2'}$ 1.8 Hz, H-1′), 4.93–4.40 (m, 10 H, $5\times -CH_2Ph$), 4.40 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.39–4.12 (m, 2 H, $-CH_2CH{=}CH_2$), 4.10 (dd, 1 H, $J_{4,5}$ 1.8 Hz, H-4), 3.96 (dd, 1 H, $J_{3',4'}$. 9.8 Hz, H-3′), 3.84 (dd, 1 H, $J_{5',6'}$ 6.1 Hz, H-5′), 3.71 (dd, 1 H, $J_{2,3}$ 9.8 Hz, H-2), 3.65 (m, 2 H, H-6), 3 56 (t, 1 H, $J_{5,6}$ 6.1 Hz, H-5), 3.49 (dd, 1 H, $J_{3,4}$ 3.1 Hz, H-3), 3.39 (t, 1 H, $J_{4',5'}$ 9.8 Hz H-4′), 2.07 (s, 3 H, CH_3), 1.25 (d, 3 H, H-6). Anal. Calcd for $C_{52}H_{58}O_{11}$: C, 72.69; H, 6.81. Found: C, 71.55; H, 6.69.

2-O-*Acetyl-3*-O-*benzyl-4*-O-*(*p-*methoxybenzyl)-*α-L-*rhamnopyranosyl-(1→4)-2,3,6-tri*-O-*benzyl-*α-D-*galactopyranosyl trichloroacetimidate* (**14**).—A mixture of compound **12** (660 mg, 0.74 mmol), $PdCl_2$ (657 mg), and NaOAc (610 mg) in 90% aq AcOH (48 mL) was stirred overnight at 35 °C. The insoluble material was filtered off, the filtrate was concentrated, and the residue was extracted with EtOAc. The extract was washed with water, satd aq $NaHCO_3$, and satd NaCl, dried (Na_2SO_4), and concentrated. The residue was chromatographed on silica gel with 25:1 benzene–acetone as eluent to give 2-*O*-acetyl-3-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-D-galactopyranose. To a solution of this compound in CH_2Cl_2 (10 mL) was added CCl_3CN (1.68 mL) and DBU (two drops) at 0 °C. After 2 h the mixture was diluted $CHCl_3$, washed with water, dried (Na_2SO_4), and concentrated. The residue was chromatographed on silica gel using 100:1 $CHCl_3$–MeOH as eluent to give **14** (128 mg, 17%).

2-O-*Acetyl-3,4-di*-O-*benzyl-*α-L-*rhamnopyranosyl-(1→4)-2,3,6-tri*-O-*benzyl-*α-D-*galactopyranosyl trichloroacetimidate* (**15**).—To a solution of compound **13** (2.73 g, 3.18 mmol) in 90% AcOH (207 mL) was added $PdCl_2$ (2.82 g) and NaOAc (4.33 g). The mixture was stirred overnight at 35 °C. The insoluble material was filtered off, the filtrate was concentrated, and the residue was extracted with EtOAc. The extract was washed with water, satd aq $NaHCO_3$, and satd NaCl, dried (Na_2SO_4), and concentrated. The residue was chromatographed on silica gel using 30:1 benzene–acetone as eluent to give 2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-D-galactopyranose. A mixture of this compound and CH_2Cl_2 (12 mL) was added to CCl_3CN (9 mL) and DBU (two drops) at 0 °C. After 2 h the mixture was diluted with $CHCl_3$, washed by water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel with 100:1 $CHCl_3$–MeOH as eluent to provide **15** (917 mg, 30%); R_f 0.85 (8:1 benzene–acetone).

Allyl 2-O-*acetyl-3*-O-*benzyl-4*-O-*(*p-*methoxybenzyl)-*α-L-*rhamnopyranosyl-(1→4)-2,3,6-tri*-O-*benzyl-*α-D-*galactopyranosyl-(1→2)-3,4-di*-O-*benzyl-*α-L-*rhamnopyranosyl-(1→4)-2,3,6-tri*-O-*benzyl-*β-D-*galactopyranoside* (**16**).—A mixture of compound **11** (32 mg, 0.04 mmol), compound **14** (51 mg, 0.05 mmol), 4 Å MS (50 mg), and CH_2Cl_2 (5 mL) was stirred under argon and then at rt in the dark. Silver triflate (1.3 mg) was added to the mixture, and stirring was continued overnight. The mixture was filtered through a pad of Celite and diluted with $CHCl_3$. The filtrate was washed with water and aq $NaHCO_3$, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography using 5:1 hexane–EtOAc as eluent to provide **16** (32 mg, 49%); R_f 0.54 (8:1 benzene–acetone); ^1H NMR data ($CDCl_3$): δ 7.36–6.83 (m, 49 H, aromatic), 6.00–5.92 (m, 1 H, –CH=), 5.60 (dd, 1 H, $J_{2,3}$ 3.1 Hz, H-2d), 5.33 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1b), 5.31–5.19 (m, 2 H, CH_2=), 5.21 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1d), 4.91–4.25 (m, 20 H, $10\times -CH_2Ph$), 4.78 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1c), 4.41–4.10 (m, 2 H, $-CH_2CH{=}CH_2$), 4.37 (dd, 1 H, $J_{1,2}$ 7.9 Hz, H-1a), 4.32 (t, 1 H, $J_{5,6}$ 7.6 Hz, H-5a), 4.23 (dd, 1 H, $J_{2,3}$ 3.1 Hz, H-2b), 4.16 (bd, 1 H, H-4c), 4.08 (bd, 1 H, H-4a), 3.95 (dd, 1 H, $J_{3,4}$ 2.5 Hz, H-3c), 3.93 (dd, 1 H, $J_{3,4}$ 9.8 Hz, H-3d), 3.90 (dd, 1 H, $J_{3,4}$ 9.8 Hz, H-3b), 3.84 (m, 1 H, $J_{5,6}$ 6.1 Hz, H-5d), 3.79 (s, 3 H, OCH_3), 3.75 (m, 1 H, $J_{5,6}$ 6.1 Hz, H-5b), 3.71 (dd, 1 H, $J_{2,3}$ 10.4 Hz, H-2c), 3.67 (dd, 1 H,

$J_{2,3}$ 9.8 Hz, H-2a), 3.65 (m, 2 H, H-6c), 3.54 (t, 1 H, $J_{5,6}$ 6.7 Hz, H-5c), 3.50 (t, 1 H, $J_{4,5}$ 9.2 Hz, H-4b), 3.45 (dd, 1 H, $J_{3,4}$ 2.4 Hz, H-3a), 3.43 (m, 2 H, H-6a), 3.37 (t, 1 H, $J_{4,5}$ 9.2 Hz, H-4d), 2.07 (s, 3 H, CH_3), 1.24 (d, 3 H, H-6b), 1.21 (d, 3 H, H-6d). ^{13}C NMR data ($CDCl_3$): δ 103.0 ($J_{C\text{-}1,\ H\text{-}1}$ 157 Hz, C-1a), 99.0 ($J_{C\text{-}1,\ H\text{-}1}$ 174 Hz, C-1d), 97 9 ($J_{C\text{-}1,\ H\text{-}1}$ 170 Hz, C-1b), 95.5 ($J_{C\text{-}1,\ H\text{-}1}$ 168 Hz, C-1c). Anal. Calcd for $C_{52}H_{58}O_{11}$: C, 72.69; H, 6.81. Found: C, 71.55; H, 6.69. Anal. Calcd for $C_{100}H_{110}O_{21}$: C, 62.88; H, 6.73. Found: C, 62.94; H, 6.79.

Allyl 2-O-acetyl-3,4-di-O-benzyl-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-O-benzyl-α-D-galactopyranosyl-(1→2)-3-O-benzyl-4-O-(p-methoxybenzyl)-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (**17**).—A mixture of compound **10** (479 mg, 0.57 mmol), compound **15** (917 mg, 0.95 mmol), 4 Å MS (1.05 g), and dry CH_2Cl_2 (15 mL) was stirred for 2 h under an argon atmosphere at rt in the dark. Silver triflate (36 mg) was then added, and the mixture was stirred overnight. The mixture was diluted with $CHCl_3$, filtered, washed with water and aq $NaHCO_3$, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography using 5:1 hexane–EtOAc as eluent to give **17** (621 mg, 67%); R_f 0.54 (8:1 benzene–acetone); ^{1}H NMR data ($CDCl_3$): δ 7.36–6.81 (m, 49 H, aromatic), 6.00–5.92 (m, 1 H, –CH=), 5.60 (dd, 1 H, $J_{2,3}$ 3.1 Hz, H-2d), 5.35 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1b), 5.35–5.19 (m, 2 H, CH_2=), 5.23 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1d), 4.92–4.26 (m, 20 H, 10 × –CH_2Ph), 4.91 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1c), 4.45–4.10 (m, 2 H, –CH_2CH=CH_2), 4.37 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1a), 4.32 (t, 1 H, $J_{5,6}$ 6.7 Hz, H-5a), 4.23 (bd, 1 H, $J_{2,3}$ 3.1 Hz, H-2b), 4.17 (bd, 1 H, H-4), 4.07 (bd, 1 H, H-4a), 3.95 (dd, 1 H, $J_{3,4}$ 3.1 Hz, H-3c), 3.93 (dd, 1 H, $J_{3,4}$ 9.8 Hz, H-3d), 3.89 (dd, 1 H, $J_{3,4}$ 9.8 Hz, H-3b), 3.85 (m, 1 H, $J_{5,6}$ 6.1 Hz, H-5d), 3.76 (s, 3 H, OCH_3), 3.74 (m, 1 H, $J_{5,6}$ 6.1 Hz, H-5b), 3.71 (dd, 1 H, $J_{2,3}$ 10.4 Hz, H-2c), 3.67 (t, 1 H, $J_{2,3}$ 8.5 Hz, H-2a), 3.66 (m, 2 H, H-6c), 3.54 (t, 1 H, $J_{5,6}$ 6.1 Hz, H-5c), 3.49 (t, 1 H, $J_{4,5}$ 9.2 Hz, H-4b), 3.44 (dd, 1 H, $J_{3,4}$ 3.1 Hz, H-3a), 3.42 (m, 2 H, H-6a), 3.39 (t, 1 H, $J_{4,5}$ 9.2 Hz, H-4d), 2.07 (s, 3 H, CH_3), 1.23 (d, 3 H, H-6b), 1.22 (d, 3 H, H-6d). ^{13}C NMR data ($CDCl_3$): δ 169.9 (C=O), 103.1 ($J_{C\text{-}1,\ H\text{-}1}$ 159 Hz, C-1a), 98.9, 97.9 ($J_{C\text{-}1,\ H\text{-}1}$ 174 Hz, $J_{C\text{-}1,\ H\text{-}1}$ 176 Hz, C-1b, C-1d), 95.5 ($J_{C\text{-}1,\ H\text{-}1}$ 170 Hz, C-1c), 55 2 (OCH_3), 21.1 (CH_3CO), 18.1, 18.1 (C-6b, C-6d). Anal. Calcd for $C_{100}H_{110}O_{21}$: C, 62.88; H, 6.73. Found C, 62.79; H, 6.80.

Allyl 3-O-benzyl-4-O-(p-methoxybenzyl)-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-O-benzyl-α-D-galactopyranosyl-(1→2)-3,4-di-O-benzyl-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (**18**).—To a mixture of compound **16** (32 mg, 0.024 mmol) in MeOH (5 mL) was added NaOMe (20 mg). The mixture was stirred for 2 h at rt, then neutralized with Amberlite IR-120B (H^+), filtered, and evaporated to give **18** (29 mg, 93%); Anal. Calcd for $C_{98}H_{108}O_{20}$: C, 73.30; H, 6.78. Found: C, 73.39; H, 6.84.

Allyl 3,4-di-O-α-L-rhamnopyranoyl-(1→4)-2,3,6-tri-O-benzyl-α-D-galactopyranosyl-(1→2)-3-O-benzyl-4-O-(p-methoxybenzyl)-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (**19**).—To a solution of compound **17** (39 mg, 0.024 mmol) in MeOH (5 mL) was added NaOMe (20 mg), and the mixture was stirred at rt for 2 h. The mixture was neutralized with Amberlite IR-120B (H^+), filtered, and concentrated to give **19** (36 mg, 93%); Anal. Calcd for $C_{98}H_{108}O_{20}$: C, 73.30; H, 6.78. Found: C, 73.21; H, 6.82.

Propyl O-α-L-rhamnopyranosyl-(1→4)-O-α-D-galactopyranosyl-(1→2)-O-α-L-rhamnopyranosyl-(1→4)-O-β-D-galactopyranoside (**20**).—To a solution of compound **19** (32 mg, 0.02 mmol) in MeOH (1 mL) was added 10% Pd–C (18.7 mg). The mixture was stirred overnight under H_2, and then filtered and concentrated. The residue was chromatographed on IATROBEADS using 5:3 $CHCl_3$–MeOH as eluent to provide **20** (13 mg, 74%); ^{1}H NMR data (CD_3OD): δ 5.27 (bd, 1 H, H-1d), 5.18 (bd, 1 H, H-1b), 4.99 (d, 1 H, $J_{1,2}$ 7.2 Hz, H-1c), 4.22 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1a), 1.64 (m, 2 H, –$CH_2CH_2CH_3$), 1.28, 1.25 (each d, 6 H, H-6b, H-6d), 0.95 (t, 3 H, –$CH_2CH_2CH_3$). ^{13}C NMR data (CD_3OD): δ 105.0 (C-1a), 103.4 (C-1b), 101.1 (C-1d), 99.7 (C-1c), 24.0 ($CH_2CH_2CH_3$), 18.2,

18.0 (C-1b, C-1d), 10.8 ($CH_2CH_2CH_3$). Anal. Calcd for $C_{27}H_{48}O_{19}$: C, 47.93; H, 7.15. Found: C, 47.85; H, 7.21.

Propyl O-α-L-*rhamnopyranosyl-(1→4)*-O-*(α*-D-*galactopyranosyluronic acid)-(1→2)*-O-α-L-*rhamnopyranosyl-(1→4)*-O-*(β*-D-*galactopyranosid)uronic acid* (**21**).—A solution of compound **20** (18.8 mg, 0.028 mmol), KBr (0.6 mg), and 2,2,6,6-tetramethylpiperidine 1-oxide (TEMPO) (0.6 mg) in satd aq $NaHCO_3$ (0.3 mL) was stirred at rt, while a solution of NaOCl (0.37 mL) was added dropwise over a period of 1 h. The mixture was neutralized with Amberlite IR-120B (H^+), filtered, and concentrated. The residue was chromatographed using Sephadex LH-20 using water as eluent to remove reagents, and then by HPLC using water as eluent to provide **21** (10 mg, 50%); ^{1}H NMR data (D_2O): δ 5.21 (bd, 1 H, H-1d), 5.06 (bd, 1 H, H-1b), 1.63 (m, 2 H, $-CH_2CH_2CH_3$), 1.23, 1.21 (each d, 6 H, H-6b, H-6c), 0.92 (t, 3 H, $-CH_2CH_2CH_3$). ^{13}C NMR data (D_2O): δ 181.7, 180.9 (C-6a, C-6c), 104.6 (C-1a), 103.3 (C-1b), 102.4 (C-1d), 100.9 (C-1c), 83.9, 83.6 (C-4a, C-4c), 24.8 ($CH_2CH_2CH_3$), 19.4, 19.2 (C-1b, C-1d), 12.4 ($CH_2CH_2CH_3$). MALDI-TOFMS: Calcd for $C_{27}H_{44}O_{21}$: m/z 704.6. Found: m/z 771.6 $[M + 3\ Na - 2\ H]^+$.

Acknowledgements

The authors would like to thank Miss T. Naito for performing the microanalyses at Nagoya City University, Nagoya, Japan. This work was supported by a Grant-in-Aid for Scientific Research (No. 09672156) from the Ministry of Education, Science, Sports and Culture of Japan.

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