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Carbohydrate Research 295 (1996) 235–243

CARBOHYDRATE RESEARCH

Note

Synthesis of glycofuranosides from *S*-glycofuranosyl dithiocarbonates (xanthates) and dithiocarbamates

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Received 5 May 1996; accepted in revised form 4 September 1996

Abstract

Coupling reactions between an anomeric mixture of *S*-ribofuranosyl *N*,*N*-diethyldithiocarbamate (**1b**) as the donor and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose or 1,6-anhydro-3,4-*O*-isopropylidene-β-D-galactopyranose as the acceptor in the presence of silver triflate afforded β-D-ribofuranosyl disaccharides in good yield. Application of this glycosidation methodology for the synthesis of alkylglycofuranoside derivatives of D-xylofuranose and L-arabinofuranose resulted in the 1,2-*trans* configurated products with moderate to high stereoselectivity. © 1996 Elsevier Science Ltd.

Keywords: Glycosylation; Glycofuranosyl donors; Dithiocarbonates; Dithiocarbamates; Glycofuranosides

Stereoselective glycosylation under mild conditions is one of the basic problems in carbohydrate chemistry. Recently, a number of methods for the synthesis of glycopyranosides have been reported [1–4]. A limited number of glycofuranoside syntheses are known, however [5,6]. Conventionally, they involve activation of a suitable leaving group at C-1 of the glycosyl donor by use of a strong acid like trifluoromethanesulfonic (triflic) anhydride [5,7,8], triflic acid [9], or trimethylsilyl trifluoromethanesulfonate [10]. It is well known that glycofuranosides are very sensitive to acids and under such conditions they can isomerize. On the other hand, the use of triflic acid derivatives renders the reaction medium strongly acidic, which causes problems with acid-labile substrates. Looking for the effective procedures for stereoselective synthesis of glycofu-

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PII S0008-6215(96)00224-8

ranosides under mild reaction conditions, we have turned our attention on the sugar *S*-glycosyl dithiocarbonates and dithiocarbamates. In synthetic carbohydrate chemistry they have been introduced as reactive glycopyranosyl donors [11–13].

Recently, we have reported a simple and effective procedure for the preparation of glycosyl dithiocarbonates and dithiocarbamates derivatives of L-arabinofuranose, D-ribofuranose and D-xylofuranose [14]. The present paper reports the application of the compounds as glycofuranosyl donors in glycosidation reactions.

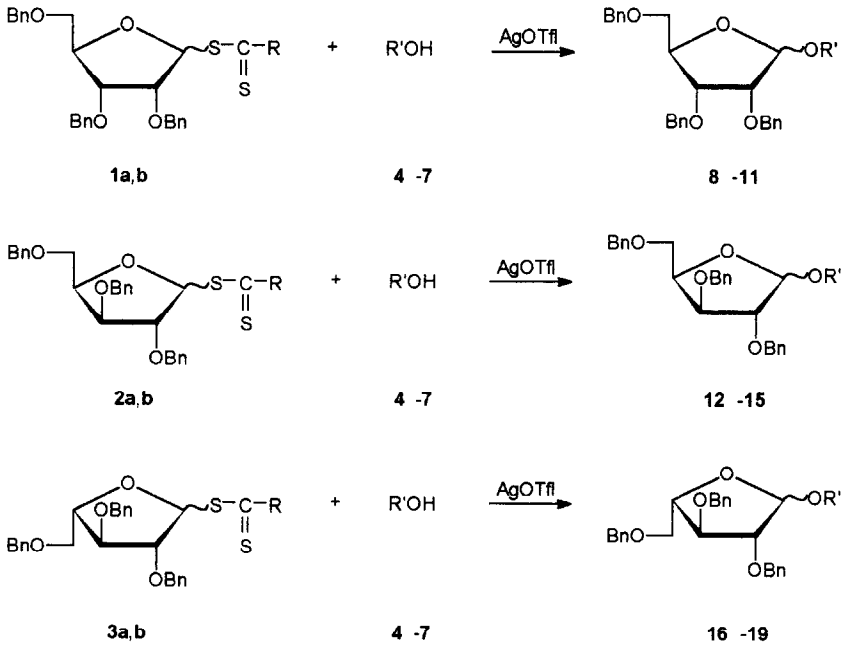
In a first approach the reaction of *O*-ethyl *S*-(2,3,5-tri-*O*-benzyl-D-ribofuranosyl) dithiocarbonate **(1a)** ($\alpha:\beta = 3:4$) and *N*,*N*-diethyl *S*-(2,3,5-tri-*O*-benzyl-D-ribofuranosyl) dithiocarbamate **(1b)** ($\alpha:\beta = 3:1$) with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **(4)** as a model glycosyl acceptor was examined using neutral salts of trifluoromethanesulfonic acid as promoter and 4 Å molecular sieves as dehydrating agent in toluene (Scheme 1). After screening a variety of salts, glycosidation was found to proceed in a few minutes with silver triflate. The β-D-ribofuranosyl disaccharide was isolated as the main product in good yield. An attempt to prepare the disaccharide in the absence of a thiophilic salt (tetraethylammonium triflate was used) failed, and glycosides were not detected (TLC).

The effect of solvents was then examined. The best results were obtained in non-polar toluene. When more polar solvents like diethyl ether or acetonitrile were used, a complex mixture of products was formed (TLC). The reaction is practically independent on the temperature. It proceeded smoothly at room temperature as well as at -78 °C, and the products were obtained in good yield and with high stereoselectivity. The structures of the furanosides have been fully characterized through ^{1}H and ^{13}C NMR spectra and optical rotation data.

Irrespective of the factors which could affect the final composition of anomers, the possibility of product equilibration could be ruled out. Thus, when a mixture of α- and β-D-ribofuranosides ($\alpha:\beta = 3:1$) was stirred with triflic acid and silver triflate for 60 min. HPLC analysis of the reaction mixture showed that α-D-ribofuranoside did not undergo anomerization to the more stable β-anomer and the composition of the mixture did not change. Therefore, the formation of glycofuranosides under the described conditions must be kinetically controlled. When the glycosylation reaction takes place through the ionic intermediate (ion-pair), selectivity appears to be influenced by the addition of strong acids salts [5,11,15]. Thus, when the glycosidation of tri-*O*-benzyl-D-ribofuranose with alcohols was carried out in the presence of lithium perchlorate, a high selectivity for the α-anomer was reported [5]. However, when we examined the influence of lithium perchlorate on the selectivity of the reaction between **1a** and **4**, it was found that the 1,2-*trans*-ribofuranoside was obtained in 60% yield. Both yield and stereoselectivity were similar in the presence or absence of salt.

We believe that the reaction proceeds as shown in Scheme 2. The reaction of the dithiocarbonate with silver triflate could result in the formation of I, followed by nucleophilic substitution. In a non-polar solvent, like toluene, the formation of the ionic intermediates (the intimate ion pair) II and III is probably delayed.

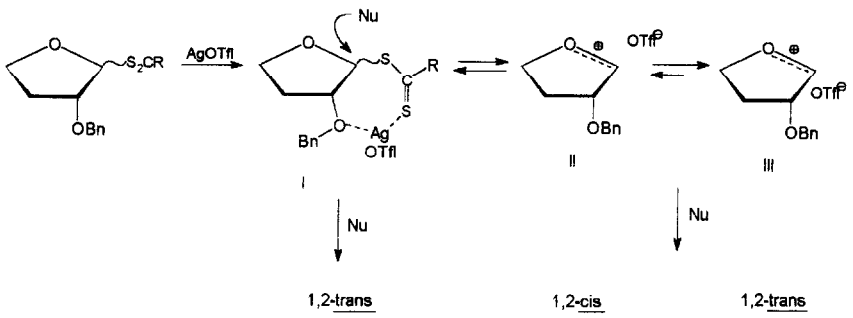
Glycosylation with dithiocarbamate **1b** gave the β-glycoside predominantly, whereas the reaction using the dithiocarbonate **1a** afforded a mixture of anomers. The reaction of **1a** and **1b** with other glycosyl acceptors like 1,6-anhydro-3,4-*O*-isopropylidene-β-D-



Scheme 1.

galactopyranose (**5**), 1,2-*O*-isopropylidene-*sn*-glycerol (**6**), and cholesterol (**7**) was also examined, and these results are summarized in Table 1. In all cases, the reaction proceeded smoothly under mild conditions with good yield and β-ribofuranosides were formed with moderate to high stereoselectivity.

To further demonstrate the efficiency of the proposed methodology, *S*-glycosyl-*N*,*N*-diethyldithiocarbamates and *O*-ethyl *S*-glycosyl dithiocarbonates derivatives of D-xylo-



Scheme 2.

furanose and L-arabinofuranose were treated with primary hydroxyl group (**4**, **6**) and secondary hydroxyl group acceptors (**5**, **7**). The glycosylation provided the 1,2-*trans*-glycofuranosides with moderate to high stereoselectivity. The stereochemical outcome of the reaction can be modulated, to some extent, by selection of the glycosyl donor. Thus, reaction of dithiocarbonate **1a** with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**4**)

Table 1
Preparation of glycofuranosides

Donor	Acceptor	Reaction time (min)	Yield (%)	Relative proportion of anomers ($\alpha:\beta$)
1a	**4**	10	64	2:3
	5	10	69	β
	6	10	92	1:2
	7	90	66	10:11
1b	**4**	5	76	β
	5	5	72	β
	6	5	84	1:15
2a	**4**	10	74	1:5
	5	10	82	1:5
	6	10	87	4:3
2b	**4**	5	75	1:2
	5	10	72	2:3
	6	10	85	1:1
	7	90	64	1:2
3a	**4**	5	76	4:3
	5	5	69	4:1
	6	10	73	4:3
3b	**4**	10	64	7:2
	5	5	70	3:1
	6	5	79	4:3
	7	90	63	2:1

afforded an anomeric mixture of glycosides (2:3) whereas in the case of the dithiocarbamate **1b**, the glycosylation gave the corresponding β-D-isomer predominantly.

These results clearly demonstrate that *S*-glycofuranosyl dithiocarbonates and dithiocarbamates can serve as potential glycosyl donors in carbohydrate chemistry and we are currently applying this methodology to the synthesis of other oligosaccharides.

1. Experimental

General methods.—Optical rotations were measured at room temperature with a Perkin–Elmer 141 Polarimeter using a sodium vapour lamp. ^1H and ^{13}C NMR spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) on a Varian 200 Gemini spectrometer (^1H, 200 MHz; ^{13}C, 50 MHz). Microanalyses were obtained on a Perkin–Elmer 240° analyzer. TLC was performed on precoated plates of Silica Gel $60F_{254}$ (E. Merck), using 8:1 benzene–EtOAc and detection by charring with sulfuric acid. Chromatographic purifications used Silica Gel 60 (Merck, 0.063–0.2 mm). HPLC was performed with a Multiwavelengths Detector and a Nukleosil 100 column (4.6 mm × 25 cm) that contained a C-18 packing (5 μm). The flow rate was 1.5 mL/min (mobile phase 15:85 water–MeOH). All glycosylation reactions were carried out in anhydrous solvents. All organic solutions were concentrated under reduced pressure at 40 °C.

S-Glycofuranosyl *N,N*-diethyldithiocarbamates and *O*-ethyl *S*-glycofuranosyl dithiocarbonates [14], 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**4**) [16], and 1,6-anhydro-3,4-*O*-isopropylidene-β-D-galactopyranose (**5**) [17] were prepared as described in the literature. 1,2-O-Isopropylidene-*sn*-glycerol (**6**), cholesterol (**7**), silver triflate and solvents were commercially available (Aldrich, Fluka, Merck, POCh) and used without purification.

General procedure for glycosylations.—The promoter (silver triflate 62 mg, 0.24 mM) was added to a stirred (0.5 h) suspension of the donor (**1–3**, 0.2 mM) and acceptor (**4–7**, 0.2 mM) in toluene (10 mL) at room temperature in the presence of molecular sieves 4 Å (40 mg) and the reaction was monitored by TLC. When the reaction was complete (see Table 1) the mixture was filtered and diluted with toluene (10 mL). The filtrate was washed with an aq satd soln of $NaHCO_3$ (3 times) and then with water, dried (Na_2SO_4) and concentrated. Column chromatography (9:1 hexane–EtOAc or 25:1 benzene–Et_2O) of the residue on silica gel afforded the glycosides and disaccharides.

1,2:3,4-Di-O-isopropylidene-6-O-(2,3,5-tri-O-benzyl-α-D-ribofuranosyl)-α-D-galactopyranose (**8α**).—Syrup, $[\alpha]_D^{20}$ +30.56° (*c* 1.28, $CHCl_3$), $[\alpha]_D^{20}$ +27.8° (*c* 1.00, $CHCl_3$) lit. [6]; ^1H NMR ($CDCl_3$): δ 7.30–7.12 (m, 15 H, ArH), 5.45 (d, 1 H, $J_{1,2}$ 4.96 Hz, H-1), 5.06 (d, 1 H, $J_{1',2'}$ 3.84 Hz, H-1'), 4.69–3.25 (m, 17 H, H-2,3,4,5,6,2',3',4',5', $OCH_2Ph \times 3$), 1.45, 1.37, 1.24, 1.22 (4 s, 12 H, O_2CMe_2). ^{13}C NMR ($CDCl_3$): δ 138.3, 137.9, 137.8, 128.3–127.5 (aromatic), 108.9, 108.5 ($O_2CMe_2 \times 2$), 102.0 (C-1'), 96.3 (C-1), 81.5, 77.4, 75.3, 73.3, 72.2, 72.1, 70.7, 70.5, 70.4, 69.8, 66.5, 65.8 (C-2,3,4,5,6,2',3',4',5', $OCH_2Ph \times 3$), 25.9, 25.8, 24.9, 24.4 ($O_2CMe_2 \times 2$). Anal. Calcd for $C_{38}H_{46}O_{10}$: C, 68.86; H, 7.00. Found: C, 68.72; H, 7.12.

1,2:3,4-Di-O-isopropylidene-6-O-(2,3,5-tri-O-benzyl-β-D-ribofuranosyl)-α-D-galactopyranose (**8β**).—Syrup, $[\alpha]_D^{20}$ −13.42° (*c* 1.83, $CHCl_3$); ^1H NMR ($CDCl_3$): δ

7.30–7.17 (m, 15 H, ArH), 5.45 (d, 1 H, $J_{1,2}$ 5.12 Hz, H-1), 5.07 (s, 1 H, H-1′), 4.68–3.42 (m, 17 H, H-2,3,4,5,6,2′,3′,4′,5′, OCH_2Ph × 3), 1.43, 1.35, 1.25, 1.21 (4 s, 12 H, O_2CMe_2). ^{13}C NMR ($CDCl_3$): δ 138.4, 137.9, 137.8, 128.3–127.4 (aromatic), 109.2, 108.4 (O_2CMe_2 × 2), 105.3 (C-1′), 96.2 (C-1), 80.3, 79.3, 78.3, 73.0, 72.3, 72.0, 71.2, 71.1, 70.5, 70.4, 67.5, 66.5 (C-2,3,4,5,6,2′,3′,4′,5′, OCH_2Ph × 3), 26.1, 25.9, 24.9, 24.3 (O_2CMe_2 × 2). Anal. Calcd for $C_{38}H_{46}O_{10}$: C, 68.86; H, 7.00. Found: C, 68.81; H, 7.05.

*1,6-Anhydro-3,4-*O*-isopropylidene-2-*O*-(2,3,5-tri-*O*-benzyl-α-*D*-ribofuranosyl)-β-*D*-galactopyranose* (**9α**).—Syrup, $[\alpha]_D^{20}$ +49.3° (*c* 1.16, $CHCl_3$); ^{1}H NMR ($CDCL_3$): δ 7.37–7.18 (m, 15 H, ArH), 5.46 (s, 1 H, H-1), 5.14 (d, 1 H, $J_{1',2'}$ 3.58 Hz, H-1′), 4.75–3.34 (m, 17 H, H-2,3,4,5,6,2′,3′,4′,5′, OCH_2Ph × 3), 1.51, 1.29, (2 s, 6 H, O_2CMe_2). ^{13}C NMR ($CDCl_3$): δ 138.2, 137.8, 137.7, 128.3–127.5 (aromatic), 108.2 (O_2CMe_2), 100.5 (C-1), 99.2 (C-1′), 82.0, 77.9, 75.5, 75.1, 74.8, 73.3, 72.7, 72.3, 71.9, 69.7, 69.1, 63.1 (C-2,3,4,5,6,2′,3′,4′,5′, OCH_2Ph × 3), 25.7, 24.3 (O_2CMe_2). Anal. Calcd for $C_{35}H_{40}O_9$: C, 69.52; H, 6.67. Found: C, 69.72; H, 6.39.

*1,6-Anhydro-3,4-*O*-isopropylidene-2-*O*-(2,3,5-tri-*O*-benzyl-β-*D*-ribofuranosyl)-β-*D*-galactopyranose* (**9β**).—Syrup, $[\alpha]_D^{20}$ −16.0° (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.29–7.17 (m, 15 H, ArH), 5.38 (s, 1 H, H-1), 5.04 (s, 1 H, H-1′), 4.64–3.39 (m, 17 H, H-2,3,4,5,6,2′,3′,4′,5′, OCH_2Ph × 3), 1.44, 1.26, (2 s, 6 H, O_2CMe_2). ^{13}C NMR ($CDCl_3$): δ 137.9, 137.8, 137.7, 128.3–127.5 (aromatic), 108.5 (O_2CMe_2), 104.5 (C-1′), 100.5 (C-1), 80.7, 80.1, 77.8, 74.9, 73.9, 73.2, 72.6, 72.5, 71.9, 70.1, 69.2, 63.1 (C-2,3,4,5,6,2′,3′,4′,5′, OCH_2Ph × 3), 25.8, 24.4 (O_2CMe_2). Anal. Calcd for $C_{35}H_{40}O_9$: C, 69.52; H, 6.67. Found: C, 69.32; H, 6.21.

*1,2-*O*-Isopropylidene-3-*O*-(2,3,5-tri-*O*-benzyl-α-*D*-ribofuranosyl)*-sn-*glycerol* (**10α**).—Syrup, $[\alpha]_D^{20}$ +84.41° (*c* 0.79, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.38–7.18 (m, 15 H, ArH), 5.05 (d, 1 H, $J_{1',2'}$ 3.84 Hz, H-1′), 4.72–3.30 (m, 16 H, H-1,2,3,2′,3′,4′,5′, OCH_2Ph × 3), 1.42, 1.35 (2 s, 6 H, O_2CMe_2). ^{13}C NMR ($CDCl_3$): δ 138.2, 137.8, 137.7, 128.3–127.6 (aromatic), 109.3 (O_2CMe_2), 101.4 (C-1′), 81.9, 77.5, 75.2, 74.6, 73.4, 72.5, 72.3, 69.9, 68.8, 67.4 (C-1,2,3,2′,3′,4′,5′, OCH_2Ph × 3), 26.9, 25.4 (O_2CMe_2). Anal. Calcd for $C_{31}H_{38}O_7$: C, 71.24; H, 7.33. Found: C, 71.32; H, 7.11.

*1,2-*O*-isopropylidene-3-*O*-(2,3,5-tri-*O*-benzyl-β-*D*-ribofuranosyl)-sn-glycerol* (**10β**).—Syrup, $[\alpha]_D^{20}$ +15.43° (*c* 1.75, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.36–7.22 (m, 15 H, ArH), 5.03 (s, 1 H, H-1′), 4.73–3.30 (m, 16 H, H-1,2,3,2′,3′,4′,5′, OCH_2Ph × 3), 1.38, 1.33 (2 s, 6 H, O_2CMe_2). ^{13}C NMR ($CDCl_3$): δ 138.2, 137.8, 137.7, 128.3–127.6 (aromatic), 109.4 (O_2CMe_2), 105.3 (C-1′), 80.4, 79.5, 78.1, 74.7, 73.1, 72.4, 70.8, 68.6, 67.8, 66.4 (C-1,2,3,2′,3′,4′,5′, OCH_2Ph × 3), 26.7, 25.3 (O_2CMe_2). Anal. Calcd. for $C_{31}H_{38}O_7$: C, 71.24; H, 7.33. Found: C, 71.01; H, 7.56.

*Cholesteryl 2,3,5-tri-*O*-benzyl-α,β-*D*-ribofuranoside* (**11**).—Syrup, $[\alpha]_D^{20}$ +31.25° (*c* 0.80, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.16 (s, 1 H, 0.52 H-1′β), 5.15 (d, 1 H, $J_{1',2'}$ 4.06 Hz, 0.48 H-1′α). ^{13}C NMR ($CDCl_3$): δ 141.1, 140.4 (C-5), 138.5, 138.3, 138.0, 137.9, 128.4–127.5 (aromatic), 121.4, 120.3 (C-6), 103.4 (C-1′β), 99.6 (C-1′α), 81.1, 80.2, 78.6, 77.5, 77.3, 75.2, 73.3, 73.1, 72.3, 72.1, 71.6, 69.9, (C-3,2′,3′,4′,5′, OCH_2Ph × 3), 56.7, 56.1, (C-14,17), 50.1 (C-9), 42.3, 40.2 (C-4,13), 39.8, 39.5, 38.5 (C-12,24), 37.3, 36.7, 36.6, 36.2, 35.8 (C-1,10,22,20), 31.9, 29.5 (C-7,8,2), 28.2, 27.9 (C-16,25), 24.3,

23.8 (C-15,23), 22.8, 22.5 (C-27,26), 21.0 (C-11), 19.4, 19.3 (C-19), 18.7 (C-21), 11.8 (C-18). Anal. Calcd. for $C_{53}H_{72}O_5$: C, 80.67; H, 9.19. Found: C, 80.29; H, 8.87.

1,2:3,4-Di-O-isopropylidene-6-O-(2,3,5-tri-O-benzyl-α,β-D-xylofuranosyl)-α-D-galactopyranose (**12**).—Syrup, $[\alpha]_D^{20}$ −15.98° (*c* 5.83, $CDCl_3$); ^1H NMR ($CDCl_3$): δ 7.37–7.20 (m, 15 H, ArH), 5.55 (d, 1 H, $J_{1,2}$ 4.92 Hz, H-1), 5.52 (d, 1 H, $J_{1,2}$ 4.91 Hz, H-1), 5.15 (d, 1 H, $J_{1',2'}$ 1.28 Hz, 0.67 H-1′β), 5.11 (d, 1 H, $J_{1',2'}$ 4.27 Hz, 0.33 H-1′α), 4.74–3.56 (m, 17 H, H-2,3,4,5,6,2′,3′,4′,5′, OCH_2Ph × 3), 1.51, 1.50, 1.45, 1.42, 1.32, 1.30, 1.28, 1.25 (8 s, 12 H, O_2CMe_2). ^{13}C NMR ($CDCl_3$): δ 138.5, 138.4, 138.3, 138.0, 137.9, 137.8, 128.4–127.4 (aromatic), 109.3, 109.1, 108.5 (O_2CMe_2 × 2), 107.4 (C-1′β), 99.0 (C-1′α), 96.4 (C-1), 86.4, 83.9, 82.0, 81.7, 80.0, 76.2, 73.4, 72.4, 72.0, 71.8, 71.3, 70.8, 70.7, 70.6, 69.9, 69.3, 67.8, 67.3, 66.1, 65.6 (C-2,3,4,5,6,2′,3′,4′,5′, OCH_2Ph × 3), 26.1, 26.0, 25.0, 24.9, 24.6, 24.4 (O_2CMe_2 × 2). Anal. Calcd. for $C_{38}H_{46}O_{10}$: C, 68.86; H, 7.00. Found: C, 68.78; H, 6.89.

1,6-Anhydro-3,4-O-isopropylidene-2-O-(2,3,5-tri-O-benzyl-α-D-xylofuranosyl)-β-D-galactopyranose (**13α**).—Syrup, $[\alpha]_D^{20}$ +25.58° (*c* 3.33, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.38–7.27 (m, 15 H, ArH), 5.36 (s, 1 H, H-1), 5.12 (d, 1 H, $J_{1',2'}$ 4.27 Hz, H-1′), 4.74–3.55 (m, 17 H, H-2,3,4,5,6,2′,3′,4′,5′, OCH_2Ph × 3), 1.51, 1.28 (2 s, 6 H, O_2CMe_2). ^{13}C NMR ($CDCl_3$): δ 138.5, 137.9, 137.8, 128.5–127.4 (aromatic), 108.3 (O_2CMe_2), 100.7 (C-1), 99.8 (C-1′), 86.9, 83.9, 81.6, 75.9, 74.8, 73.3, 72.2, 72.1, 71.9, 69.4, 69.2, 63.1 (C-2,3,4,5,6,2′,3′,4′,5′, OCH_2Ph × 3), 25.8, 24.3 (O_2CMe_2). Anal. Calcd. for $C_{35}H_{40}O_9$: C, 69.52; H, 6.67. Found: C, 69.23; H, 6.27.

1,6-Anhydro-3,4-O-isopropylidene-2-O-(2,3,5-tri-O-benzyl-β-D-xylofuranosyl)-β-D-galactopyranose (**13β**).—Syrup, $[\alpha]_D^{20}$ −38.05° (*c* 3.75, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.39–7.26 (m, 15 H, ArH), 5.62 (s, 1 H, H-1), 5.22 (d, 1 H, $J_{1',2'}$ 1.28 Hz, H-1′), 4.67–3.56 (m, 17 H, H-2,3,4,5,6,2′,3′,4′,5′, OCH_2Ph × 3), 1.56, 1.37 (2 s, 6 H, O_2CMe_2). ^{13}C NMR ($CDCl_3$): δ 138.3, 137.9, 137.6, 128.4–127.5 (aromatic), 108.5 (O_2CMe_2), 106.6 (C-1′), 100.7 (C-1), 86.9, 81.6, 80.4, 75.9, 74.5, 73.4, 72.2, 72.1, 71.9, 69.4, 69.3, 63.1 (C-2,3,4,5,6,2′,3′,4′,5′, OCH_2Ph × 3), 25.8, 24.4 (O_2CMe_2). Anal. Calcd. for: $C_{35}H_{40}O_9$: C, 69.52; H, 6.67. Found: C, 69.39; H, 6.82.

1,2-O-Isopropylidene-3-O-(2,3,5-tri-O-benzyl-α-D-xylofuranosyl)-sn-*glycerol* (**14α**).—Syrup, $[\alpha]_D^{20}$ +50.21° (*c* 3.9, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.39–7.22 (m, 15 H, ArH), 5.01 (d, 1 H, $J_{1',2'}$ 4.27 Hz, H-1′), 4.68–3.49 (m, 16 H, H-1,2,3,2′,3′,4′,5′, OCH_2Ph × 3), 1.42, 1.36 (2 s, 6 H, O_2CMe_2). ^{13}C NMR ($CDCl_3$): δ 138.2, 138.1, 137.7, 128.4–127.5 (aromatic), 109.4 (O_2CMe_2), 99.9 (C-1′), 83.9, 81.5, 77.2, 76.1, 74.8, 73.4, 72.5, 69.3, 69.1, 67.0 (C-1,2,3,2′,3′,4′,5′, OCH_2Ph × 3), 26.8, 25.4 (O_2CMe_2). Anal. Calcd. for $C_{31}H_{38}O_7$: C, 71.24; H, 7.33. Found: C, 71.51; H, 7.05.

1,2-O-Isopropylidene-3-O-(2,3,5-tri-O-benzyl-β-D-xylofuranosyl)-sn-*glycerol* (**14β**).—Syrup, $[\alpha]_D^{20}$ −26.61° (*c* 1.23, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.40–7.21 (m, 15 H, ArH), 5.06 (d, 1 H, $J_{1',2'}$ 1.28 Hz, H-1′), 4.64–3.40 (m, 16 H, H-1,2,3,2′,3′,4′,5′, OCH_2Ph × 3), 1.40, 1.35 (2 s, 6 H, O_2CMe_2). ^{13}C NMR ($CDCl_3$): δ 138.2, 138.1, 137.5, 128.5–127.5 (aromatic), 109.2 (O_2CMe_2), 107.2 (C-1′), 81.7, 77.4, 76.1, 74.4, 73.4, 71.9, 69.6, 68.7, 68.1, 66.60 (C-1,2,3,2′,3′,4′,5′, OCH_2Ph × 3), 26.7, 25.5 (O_2CMe_2). Anal. Calcd. for $C_{31}H_{38}O_7$: C, 71.24; H, 7.33. Found: C, 71.49; H, 7.21.

Cholesteryl 2,3,5-tri-O-benzyl-α,β-D-xylofuranoside (**15**).—Syrup, $[\alpha]_D^{20}$ −5.59° (*c* 3.43, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.15 (d, 1 H, $J_{1',2'}$ 2.14 Hz, 0.67 H-1′β), 5.12 (d, 1

H, $J_{1',2'}$ 4.29 Hz, 0.33 H-1′α). ^{13}C NMR ($CDCl_3$): δ 140.7, 140.6 (C-5), 138.4, 138.3, 137.9, 137.7, 128.4–127.5 (aromatic), 121.8, 120.2 (C-6), 105.2 (C-1′β), 97.9 (C-1′α), 87.5, 84.1, 81.9, 81.8, 79.4, 77.4, 77.2, 75.7, 73.4, 72.5, 72.3, 71.9, 69.9, 69.4 (C-3,2′,3′,4′,5′, $OCH_2Ph \times 3$), 56.7, 56.1, (C-14,17), 50.1 (C-9), 42.3, 40.2 (C-4,13), 39.8, 39.5, 38.7 (C-12,24), 37.3, 37.2 (C-1), 36.7, 36.6, 36.2, 35.8 (C-10,22,20), 31.9, 29.6 (C-7,8,2), 28.2, 28.1, 27.9 (C-16,25), 24.3, 23.8 (C-15,23), 22.8, 22.5 (C-27,26), 21.0 (C-11), 19.4, (C-19), 18.7 (C-21), 11.8 (C-18). Anal. Calcd. for $C_{53}H_{72}O_5$: C, 80.67; H, 9.19. Found: C, 80.83; H, 9.47.

*1,2:3,4-Di-*O*-isopropylidene-6-*O*-(2,3,5-tri-*O*-benzyl-*α,β*-*L*-arabinofuranosyl)-*α*-*D*-galactopyranose* (**16**).—Syrup, $[\alpha]_D^{20}$ −31.28° (*c* 3.50, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.39–7.19 (m, 15 H, ArH), 5.55 (d, 1 H, $J_{1,2}$ 5.39 Hz, H-1), 5.52 (d, 1 H, $J_{1,2}$ 5.50 Hz, H-1), 5.21 (d, 1 H, $J_{1',2'}$ 1.02 Hz, 0.78 H-1′α), 5.06 (d, 1 H, $J_{1',2'}$ 3.68 Hz, 0.22 H-1′β), 4.74–3.53 (m, 17 H, H-2,3,4,5,6,2′,3′,4′,5′, $OCH_2Ph \times 3$), 1.52, 1.43, 1.32, 1.30 (4 s, 12 H, O_2CMe_2). ^{13}C NMR ($CDCl_3$): δ 138.1, 137.9, 137.8, 137.6, 128.3–127.5 (aromatic), 109.2, 109.1, 108.5 ($O_2CMe_2 \times 2$), 106.5 (C-1′α), 100.7 (C-1′β), 96.3 (C-1), 87.8, 84.1, 83.5, 83.3, 80.4, 73.3, 72.6, 72.2, 71.9, 71.8, 71.7, 71.6, 71.2, 70.6, 70.5, 70.4, 69.7, 67.8, 66.5, 65.7, 65.4 (C-2,3,4,5,6,2′,3′,4′,5′, $OCH_2Ph \times 3$), 26.1, 25.9, 24.9, 24.8, 24.5, 24.3 ($O_2CMe_2 \times 2$). Anal. Calcd. for $C_{38}H_{46}O_{10}$: C, 68.86; H, 7.00. Found: C, 68.75; H, 6.88.

*1,6-Anhydro-3,4-*O*-isopropylidene-2-*O*-(2,3,5-tri-*O*-benzyl-*α,β*-*L*-arabinofuranosyl)-*β*-*D*-galactopyranose* (**17**).—Syrup, $[\alpha]_D^{20}$ −54.84° (*c* 0.47, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.40–7.22 (m, 15 H, ArH), 5.49 (s, 1 H, H-1), 5.32 (s, 1 H, H-1), 5.19 (d, 1 H, $J_{1',2'}$ 1.02 Hz, 0.8 H-1′α), 5.02. (d, 1 H, $J_{1',2'}$ 4.27 Hz, 0.2 H-1′β), 4.74–3.48 (m, 17 H, H-2,3,4,5,6,2′,3′,4′,5′, $OCH_2Ph \times 3$), 1.52, 1.49, 1.34, 1.24 (4 s, 6 H, O_2CMe_2). ^{13}C NMR ($CDCl_3$): δ 138.1, 138.0, 137.9, 137.5, 128.4–127.6 (aromatic), 108.6, 108.3 (O_2CMe_2), 105.9 (C-1′α), 100.7, 100.6, (C-1), 99.3 (C-1′β), 88.7, 84.1, 83.3, 82.3, 80.9, 80.1, 76.2, 75.3, 74.4, 74.3, 73.4, 73.3, 72.7, 72.5, 72.2, 72.1, 71.9, 71.7, 69.3, 69.0, 63.1 (C-2,3,4,5,6,2′,3′,4′,5′, $OCH_2Ph \times 3$), 25.8, 25.7, 24.4, 24.3 (O_2CMe_2). Anal. Calcd. for $C_{35}H_{40}O_9$: C, 69.52; H, 6.67. Found: C, 69.83; H, 6.47.

*1,2-*O*-Isopropylidene-3-*O*-(2,3,5-tri-*O*-benzyl-*α,β*-*L*-arabinofuranosyl)-*sn*-glycerol* (**18**).—Syrup, $[\alpha]_D^{20}$ −16.22° (*c* 1.80, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.40–7.19 (m, 15 H, ArH), 5.08 (d, 1 H, $J_{1',2'}$ 0.85 Hz 0.57 H-1′α), 4.94 (d, 1 H, $J_{1',2'}$ 3.80 Hz, 0.43 H-1′β), 4.72–3.41 (m, 16 H, H-1,2,3,2′,3′,4′,5′, $OCH_2Ph \times 3$), 1.41, 1.39, 1.36, 1.34 (4 s, 6 H, O_2CMe_2). ^{13}C NMR ($CDCl_3$): δ 138.1, 138.0, 137.9, 137.8, 137.6, 137.4, 128.4–127.6 (aromatic), 109.5, 109.3 (O_2CMe_2), 106.5 (C-1′α), 100.9 (C-1′β), 88.1, 84.1, 83.5, 82.9, 80.8, 80.2, 74.7, 74.4, 73.4, 72.3, 72.1, 71.9, 69.6, 68.8, 68.6, 67.6, 66.9, 66.6 (C-1,2,3,2′,3′,4′,5′, $OCH_2Ph \times 3$), 26.8, 26.7, 25.5, 25.4 (O_2CMe_2). Anal. Calcd. for $C_{31}H_{38}O_7$: C, 71.24; H, 7.33. Found: C, 71.53; H, 7.68.

*Cholesteryl 2,3,5-tri-*O*-benzyl-*α,β*-*L*-arabinofuranoside* (**19**).—Syrup, $[\alpha]_D^{20}$ −12.86° (*c* 0.52, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.21 (d, 1 H, $J_{1',2'}$ 1.02 Hz, 0.67 H-1′α), 5.06 (d, 1 H, $J_{1',2'}$ 4.11 Hz, 0.33 H-1′β). ^{13}C NMR ($CDCl_3$): δ 140.7, 140.6 (C-5), 138.2, 138.1, 138.0, 137.9, 137.7, 137.6, 128.4–127.5 (aromatic), 121.7, 120.1 (C-6), 104.2 (C-1′α), 98.9 (C-1′β), 88.8, 83.9, 83.5, 83.4, 80.1, 79.9, 76.5, 73.3, 72.9, 72.2, 72.0, 71.9, 69.6 (C-3,2′,3′,4′,5′, $OCH_2Ph \times 3$), 56.7, 56.1, (C-14,17), 50.1 (C-9), 42.3, 40.2 (C-4,13), 39.8, 39.5, 38.6 (C-12,24), 37.2, 37.1 (C-1), 36.7, 36.6, 36.1, 35.7 (C-10,22,20), 31.8,

29.7 (C-7,8,2), 28.2, 27.9 (C-16,25), 24.2, 23.8 (C-15,23), 22.8, 22.5 (C-27,26), 20.9 (C-11), 19.4, (C-19), 18.7 (C-21), 11.8 (C-18). Anal. Calcd. for $C_{53}H_{72}O_5$: C, 80.67; H, 9.19. Found: C, 80.35; H, 9.41.

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