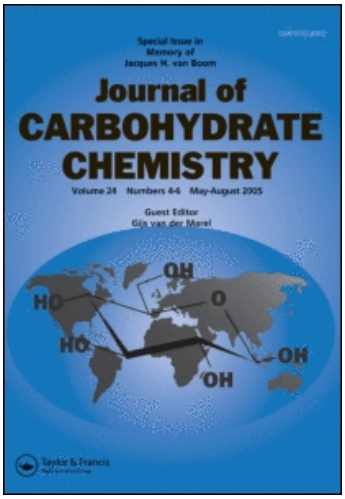

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A General Method for Stepwise Elongation of the (1→5)-α-D-Arabinofuranan Chain

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A GENERAL METHOD FOR STEPWISE ELONGATION OF THE (1→5)-α-D-ARABINOFURANAN CHAIN

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ABSTRACT

Condensation reaction of 3,5-di-O-benzoyl-1,2-O-(1-cyanobenzylidene)-β-D-arabinofuranose (2) with benzyl and allyl 2,3-di-O-benzoyl-5-O-triphenylmethyl-α-D-arabinofuranosides (5a and 5b) in methylene chloride in the presence of triphenylcarbenium tetrafluoroborate as catalyst under high vacuum gave α-(1→5)-linked dimeric D-arabinofuranoside derivatives (6a and 6b). One of the dimeric compounds (6a) was debenzoylated, triphenylmethylated, and rebenzoylated to give a dimeric homolog of 5a (8). Similarly for the preparation of 6a, 8 was condensed with 2 to provide an α-(1→5)-linked trimeric D-arabinofuranoside derivative (9). Further elongation of the glycoside chain might be possible in the same way.

INTRODUCTION

Misaki and his collaborators[1] have described that D-arabino-D-galactan linked covalently to the peptideglycan acts as a common antigen to a group of Mycobacterium, Corynebacterium, and Nocardia species and that the polysaccharide has a branched structure with

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a 5/2 ratio of D-arabinose and D-galactose. It has also been shown that α-(1→5)-D-arabinofuranan oligomers, existing as terminals of the polysaccharide side chains are responsible for the serological activity. As a result, it would be helpful to elucidate the exact chain length of the glycan with immunodeterminant activity, and to prepare a series of (1→5)-linked oligosaccharides consisting of an increasing number of D-arabinofuranosyl residues. This article deals with an attempt to develop a general method for the stepwise elongation of the (1→5)-α-D-arabinofuranan chain and some observations about the behavior of those oligosaccharides.

RESULTS AND DISCUSSION

Procedures for 1,2-*trans*-glycoside synthesis employing 1,2-orthoesters,[2] 1,2-thioorthoesters,[3] or 1,2-O-cyanoalkylidene derivatives[4] of sugars as glycosyl donors have been developed by Kochetkov and his collaborators. Recently, methyl 5-O-(α-L-arabinofuranosyl)-α-L-arabinofuranoside derivatives were prepared by the thioorthoester method.[5] We examined the applicability of the cyanoalkylidene method for the stepwise elongation of the 1,5-linked α-D-arabinofuranan chain.

2,3,5-Tri-O-benzoyl-D-arabinofuranosyl bromide (1) was prepared from the corresponding methyl α-D-arabinoside derivative by the procedure of Ness and Fletcher[6] and used immediately for subsequent reactions without any purification. The glycosyl donor, 3,5-di-O-benzoyl-1,2-O-(1-cyanobenzylidene)-β-D-arabinofuranose (2) was prepared according to literature procedures[7,8] with some modifications. The glycosyl acceptors, benzyl and allyl 2,3-di-O-benzoyl-5-O-triphenylmethyl-α-D-arabinofuranosides (5a and 5b), were prepared by the orthoester procedure as follows. The bromide 1 was treated with benzyl alcohol or allyl alcohol in the presence of 2,6-lutidine to give the 1-benzyloxybenzylidene (3a) or 1-allyloxybenzylidene derivative (3b). Compounds 3a and

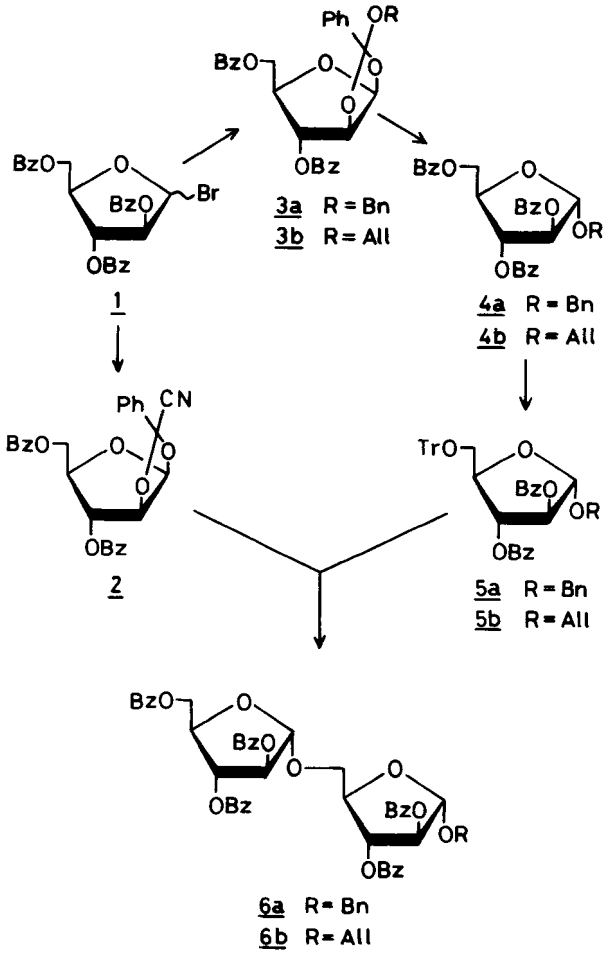

Fig. 1.

3b were again treated in nitromethane with benzyl and allyl alcohol, respectively, in the presence of mercuric bromide, giving the corresponding α-arabinofuranosides (4a and 4b) that showes anomeric protons as singlets in their ^{1}H NMR spectra. After removal of benzoates from 4a and 4b with base, the resulting compounds were triphenylmethylated on the primary hydroxyl group and rebenzoylated on the secondary hydroxyl groups to give 5a and 5b. These triphenylmethylation reactions produced some by-products (probably di-O-triphenylmethyl compounds) although the stoichiometric amount of

triphenylmethyl chloride was used. Coupling reactions between 2 and 5a or 5b were carried out in methylene chloride at 45° under high vacuum with triphenylcarbenium tetrafluoroborate as a catalyst in a modified known procedure.[4] The disaccharides (6a and 6b) were isolated by column chromatography in a yield of 33-50%. The benzyl glycoside 6a was obtained in better yield than the allyl glycoside 6b. Coupling reaction at room temperature seemed to decrease the yield of the products.

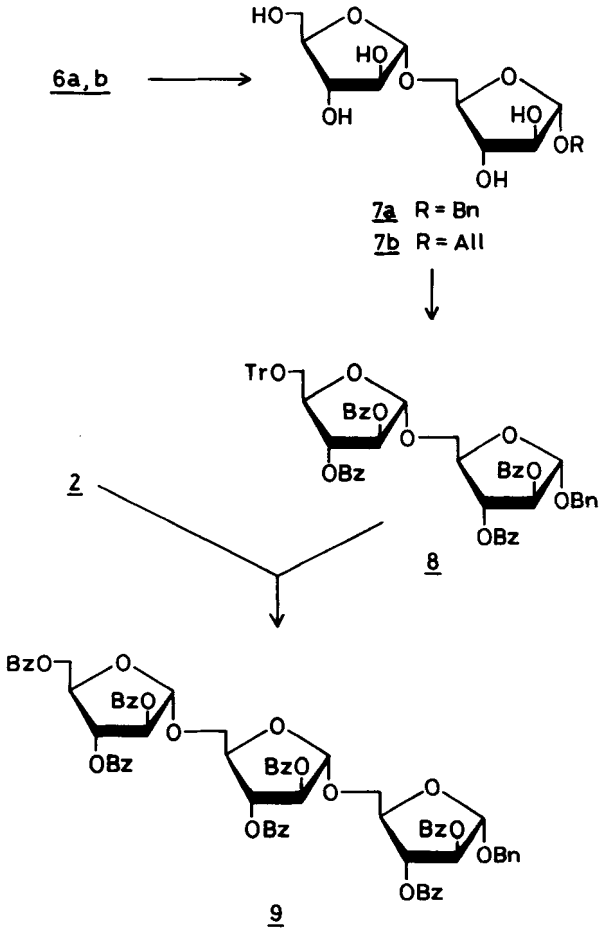

Fig. 2.

For further elongation of the sugar chain, a conversion of the disaccharide derivatives into the new glycosyl acceptors was required. This was performed in a fashion similar to the conversion of 4a,b into 5a,b. Debenzoylation of 6a and 6b with a base gave compounds 7a and 7b, respectively. At this stage, it was appropriate to test the stability of the internal glycoside bond under the reaction conditions to be employed to regenerate the reducing end of the oligosaccharides. Thus, the benzyl or the allyl group was removed from a small amount of 7a,b under the mildest conditions and the resulting free sugars were examined by HPLC. Surprisingly, deallylation of 4b with $PdCl_2$-CH_3COONa-CH_3COOH[9] gave arabinose as major product, suggesting that most of the internal glycoside bond was cleaved under these conditions; whereas catalytic hydrogenation of 4a with Pd-C gave a single product having a retention time consistent for the disaccharide. On the basis of these results, further modification of allyl glycoside 7b was given up. Compound 7a was treated with an equimolar amount of triphenylmethyl chloride and then with an excess of benzoyl chloride, giving the 5'-O-triphenylmethyl derivative (8) in 56% yield. Again, production of some by-products was observed during the triphenylmethylation reaction.

Coupling reaction between 2 and 8 was performed using the same reagents as those in the disaccharide syntheses with some variation of the reaction conditions. A combination of lower temperature and longer time (0°, 30 h) was employed to minimize the amount of side reaction products. As a result, the trisaccharide derivative (9) was obtained in 35% yield. By repeating the procedures for the conversion of 6a→ 7a→ 8, 9 should be convertible into the glycosyl acceptor for the tetrasaccharide synthesis.

In conclusion, it has been shown that the glycosidation method employing the cyanobenzylidene derivative is applicable to the stepwise elongation of the (1→5)-α-D-arabinofuranan chain, when experimental procedures are carried out with great care to prevent the cleavage of internal glycoside bonds.

EXPERIMENTAL

General Procedures. Melting points were determined with a Yamato micro melting point apparatus and are uncorrected. Optical rotations were measured at 25°C with a Parkin-Elmer Model 241MC porarimeter. The 400 MHz ^{1}H NMR spectra were recorded with JEOL GX-400 spectrometer in chloroform-d (Me_4Si as standard) unless otherwise specified. Column chromatography was performed with silica gel (Merck, 70-230 mesh) with the solvent system noted. Thin layer chromatography was conducted on precoated plates of Silica Gel 60 F_{254} (Merck). High-performance liquid chromatography was performed with a combination of Hitachi Model 635A (pump) and Shodex RI SE-11 (detector) using a Shodex S-614J column. Coupling reactions for elongation of the sugar chain were conducted at 10^{-5} mmHg in high-vacuum reaction ampoules.

3,5-Di-O-benzoyl-1,2-O-(1-cyanobenzylidene)-β-D-arabinofuranose (2). Silver cyanide (25 g) was added to a solution in xylene (260 mL) of the bromide 1 prepared from the methyl arabinoside derivative (12.5 g). The mixture was heated under gentle reflux for 2 h, cooled to room temperature, and filtered. The filtrate was concentrated in vacuo and the resulting syrupy product was dissolved in ethyl ether to give crystalline 2. After filtration, the mother liquor was concentrated and chromatographed with hexane-ethyl acetate (9:1 v/v) as eluent to give additional 2. The total yield of 2 (2.05 g) based on the methyl arabinoside derivative was 16%. mp 151-152 °C, $[\alpha]_D^{25}$ -17.9° (c 1.15, $CHCl_3$); lit.[8] mp 151 °C, $[\alpha]_D^{23}$ -20.3° (c 0.17, $CHCl_3$).

3,5-Di-O-benzoyl-1,2-O-(1-benzyloxybenzylidene)-β-D-arabinofuranose (3a). A solution of 1 prepared from methyl arabinoside tribenzoate (60 g) and 2,6-lutidine (60 mL) in benzyl alcohol (240 mL) was kept at room temperature for 20 h and then diluted with a mixture of ether (480 mL), petroleum ether (1200 mL), and water (360 mL). The organic solution was separated, washed with 2N aqueous silver nitrate and water and concentrated in vacuo. Remaining benzyl alcohol and a trace amount of 2,6-lutidine was separated

as the water azeotrope, and the water was separated as the benzene azeotrope. Crystallization twice from benzene-hexane to give 3a (23.5 g, 36%); mp 92.5-93.5 °C, $[\alpha]_D^{25}$ -9.4° (c 1.09, $CHCl_3$), NMR δ 4.31 (d, 2 H, J 7.3 Hz, H-5), 4.36 and 4.40 (d, 2 H, J 11.3 Hz, CH_2Ph), 4.64 (t, 1 H, J 7.3 Hz, H-4), 5.12 (ddd, 1 H, J 0.6, 0.9, and 4.3 Hz, H-2), 5.55 (m, 1 H, H-3), 6.32 (d, 1 H, J 4.3 Hz, H-1), 7.21-8.06 (m, 20 H, 4 Ph).

Anal. Calcd for $C_{33}H_{28}O_8$: C, 71.73; H, 5.11. Found: C, 71.64; H, 5.05.

3,5-Di-O-benzoyl-1,2-O-(1-allyloxybenzylidene)-β-D-arabinofuranose (3b). A solution of 1 prepared from the methyl arabinoside derivative (25 g) and 2,6-lutidine (25 mL) in allyl alcohol (100 mL) was kept at room temperature for 20 h and then diluted with a mixture of ether (200 mL), petroleum ether (500 mL), and water (150 mL). The organic solution was separated, washed with 2N aqueous silver nitrate and water, dried (Na_2SO_4), and concentrated in vacuo to give crystals. These were recrystallized twice from benzene-hexane to give 3b (15.9 g, 60%); mp 78-79 °C, $[\alpha]_D^{25}$ -18.1° (c 1.13, $CHCl_3$), NMR δ 3.87 (m, 2 H, $OCH_2CH=CH_2$), 4.28 (d, 2 H, J 7.3 Hz, H-5), 4.63 (t, 1 H, J 7.3 Hz, H-4), 5.12 (d, 1 H, J 4.3 Hz, H-2), 5.13 and 5.24 (m, 2 H, $OCH_2CH=CH_2$), 5.53 (d, 1 H, J 0.6 Hz, H-3), 5.85 (m, 1 H, $OCH_2CH=CH_2$), 6.35 (d, 1 H, J 4.3 Hz, H-1), 7.39-8.08 (m, 15 H, 3 Ph).

Anal. Calcd for $C_{29}H_{30}O_6$: C, 69.31; H, 5.21. Found: C, 69.03; H, 5.07.

Benzyl 2,3,5-tri-O-benzoyl-α-D-arabinofuranoside (4a). A solution of 3a (33.1 g), benzyl alcohol (124 mL), and mercuric bromide (4.3 g) in nitromethane (660 mL) was kept at room temperature for 20 h. At the end of the reaction, chloroform (500 mL) and trifluoroacetic acid (10 mL) were added and the solution was stirred for 30 min in order to decomposed the remaining orthoester. The chloroform solution was washed successively with water, saturated sodium bicarbonate solution, and water, dried ($MgSO_4$), and concentrated to a syrup, which was chromatographed with hexane-ethyl acetate (8:1 v/v) to give crystalline 4a (23.6

g, 71%); mp 89-90 °C, $[\alpha]_D^{25}$ +10.1° (c 1.04, $CHCl_3$) NMR δ4.61 (dd, 1 H, J 3.7 and 5.2 Hz, H-4), 4.67 and 4.88 (d, 2 H, J 12.2 Hz, OCH_2Ph), 4.69 (dd, 1 H, J 5.2 and 11.9 Hz, H-5a), 4.83 (dd, 1 H, J 3.7 and 11.9 Hz, H-5b), 5.40 (s, 1 H, H-1), 5.59-5.61 (m, 2 H, H-2 and H-3), 7.28-8.07 (m, 20 H, 4 Ph).

Anal. Calcd for $C_{33}H_{28}O_8$: C, 71.73; H, 5.11. Found: C, 71.69; H, 5.05.

Allyl 2,3,5-tri-O-benzoyl-α-D-arabinofuranoside (4b). A solution of 3b (5.0 g), allyl alcohol (13.5 mL), and mercuric bromide (720 mg) in nitromethane (100 mL) was kept at room temperature for 20 h. At the end of the reaction, chloroform (500 mL) and trifluoroacetic acid (10 mL) were added and the solution was stirred for 30 min in order to decomposed the remaining ortho-ester. The chloroform solution was washed successively with water, saturated sodium bicarbonate solution, and water, dried ($MgSO_4$), and concentrated to a syrup, which was chromatographed with hexane-ethyl acetate (5:1 v/v) to give 4b (4.1 g, 82%), $[\alpha]_D^{25}$ -8.2° (c 1.00, $CHCl_3$), NMR δ 4.14 and 4.33 (m, 2 H, $OCH_2CH=CH_2$), 4.61 (dt, 1 H, J 3.4 and 4.9 Hz, H-4), 4.69 (dd, 1 H, J 4.9 and 11.9 Hz, H-5a), 4.84 (dd, 1 H, J 3.4 and 11.9 Hz, H-5b), 5.23 and 5.39 (m, 2 H, $OCH_2CH=CH_2$), 5.34 (s, 1 H, H-1), 5.56 (d, 1 H, J 1.2 Hz, H-2), 5.59 (ddd, 1 H, 0.6, 1.2, and 4.9 Hz, H-3), 5.97 (m, 1 H, $OCH_2CH=CH_2$), 7.28-8.10 (m, 15 H, 3 Ph).

Anal. Calcd for $C_{29}H_{30}O_6$: C, 69.31; H, 5.21. Found: C, 69.53; H, 5.15.

Benzyl 2,3-di-O-benzoyl-5-O-triphenylmethyl-α-D-arabinofuranoside (5a). A 5% methanolic solution of sodium methoxide (20 mL) was added to the solution of 4a (20 g) in chloroform (40 mL)-methanol (200 mL) mixture. The resulting mixture was kept at room temperature for 30 min and neutralized with Dowex 50 (H^+) in water. After filtration, the filtrate was diluted with chloroform and water. The aqueous solution was separated from the organic one, washed with chloroform, and evaporated to dryness to give the debenzoylated glycoside almost quantitatively. To a solution of this product (7.95 g, 33.1 mmol) in dried pyridine

(80 mL) was added triphenylmethyl chloride (11.07 g, 39.7 mmol). The mixture was kept at room temperature for 23 h and diluted with benzene and water. The organic layer was separated, dried ($MgSO_4$), and concentrated to a syrup, which was chromatographed with benzene-ethyl acetate (6:1 v/v). The main product was treated with benzoyl chloride (54 mL) in pyridine (140 mL) and, after usual work-up, the resulting 5a was purified by column chromatography using hexane-ethyl ether (10:1 v/v) as eluent; yield 10.4 g (46% on the basis of free arabinoside); mp 114-115 °C, $[\alpha]_D^{25}$ -0.5° (c 1.07, $CHCl_3$), NMR δ 3.47 (dd, 1 H, J 5.0 and 10.1 Hz, H-5a), 3.50 (dd, 1 H, J 5.5 and 10.1 Hz, H-5b), 4.48 (q, 1 H, J 5.0 Hz, H-4), 4.63 and 4.87 (d, 2 H, J 11.9 Hz, OCH_2Ph), 5.34 (s, 1 H, H-1), 5.51 (d, 1 H, J 1.2 Hz, H-2), 5.56 (dd, 1 H, J 1.2 and 4.6 Hz, H-3), 7.17-8.03 (m, 30 H, 6 Ph).

Anal. Calcd for $C_{45}H_{38}O_7$: C, 78.24; H, 5.54. Found: C, 78.13; H, 5.46.

Allyl 2,3-di-O-benzoyl-5-O-triphenylmethyl-α-D-arabinofuranoside (5b). A 5% methanolic solution of sodium methoxide (20 mL) was added to the solution of 4b (10 g) in chloroform (10 mL)-methanol (100 mL) mixture. The resulting mixture was kept at room temperature for 30 min and neutralized with Dowex 50 (H^+) in water. After filtration, the filtrate was diluted with chloroform and water. The aqueous solution was separated from the organic one, washed with chloroform, and concentrated to dryness to give the debenzoylated glycoside almost quantitatively. To a solution of the product (43.5 g, 22.9 mmol) in dried pyridine (43.5 mL) was added triphenylmethyl chloride (7.02 g, 25.2 mmol). The mixture was kept at room temperature for 14 h and diluted with benzene and water. The organic layer was separated, dried ($MgSO_4$), and concentrated to a syrup, which was chromatographed with benzene-ethyl acetate (4:1 v/v). The main product was treated with benzoyl chloride (43 mL) in pyridine (110 mL) and, after usual work-up, the resulting 5b was purified by column chromatography using hexane-ethyl acetate (10:1 v/v) as eluent; yield 11.0 g (75% on the basis of free arabinoside); $[\alpha]_D^{25}$ -19.6°

(c 1.05, $CHCl_3$), NMR δ 3.48 (dd, 1 H, J 5.2 and 10.1 Hz, H-5a), 3.47 (dd, 1 H, J 5.2 and 10.1 Hz, H-5b), 4.12 and 4.31 (m, 2 H, $OCH_2CH=CH_2$), 4.47 (q, 1 H, J 5.2 Hz, H-4), 5.22 and 5.38 (m, 2 H, $OCH_2CH=CH_2$), 5.28 (s, 1 H, H-1), 5.46 (d, 1 H, J 1.5 Hz, H-2), 5.56 (ddd, 1 H, J 0.6, 1.5, and 5.0 Hz, H-3), 5.97 (m, 1 H, $OCH_2CH=CH_2$), 7.17-8.06 (m, 25 H, 5 Ph).

Anal. Calcd for $C_{41}H_{36}O_7$: C, 76.86; H, 5.66. Found: C, 76.97; H, 5.73.

Benzyl 2,3-di-O-benzoyl-5-O-(2,3,5-tri-O-benzoyl-α-D-arabinofuranosyl)-α-D-arabinofuranoside (6a). A solution of 5a (9.12 g, 13.2 mmol), 2 (5.85 g, 12.0 mmol), and triphenylcarbenium tetrafluoroborate (0.4 g, 1.2 mmol) in methylene chloride (50 mL) was kept at 45 °C for 80 min. The reaction was terminated by the addition of pyridine (30 mL) and methanol (60 mL), and the solution was diluted with chloroform (500 mL). The chloroform solution was washed with water, dried (Na_2SO_4), and concentrated to a syrup, which was chromatographed with hexane-ethyl acetate (6:1 v/v) to give 6a (5.39 g, 50%); $[\alpha]_D^{25}$ +11.0° (c 0.84, $CHCl_3$), NMR δ 3.99 (dd, 1 H, J 2.9 and 11.2 Hz, H-5b), 4.24 (dd, 1 H, J 4.7 and 11.2 Hz, H-5a), 4.51 (m, 1 H, H-4), 4.61 (d, 1 H, OCH_2Ph), 4.66 (dd, 1 H, J 4.7 and 11.7 Hz, H-5a'), 4.74 (m, 1 H, H-4'), 4.82-4.85 (m, 2 H, H-5b' and OCH_2Ph), 5.34 (s, 1 H, H-1), 5.46 (s, 1 H, H-1'), 5.57-5.65 (m, 4 H, H-2, H-3, H-2', and H-3'), 7.18-8.04 (m, 30 H, 6 Ph).

Anal. Calcd for $C_{52}H_{44}O_{14}$: C, 69.95; H, 4.97. Found: C, 69.83; H, 5.04.

Allyl 2,3-di-O-benzoyl-5-O-(2,3,5-tri-O-benzoyl-α-D-arabinofuranosyl)-α-D-arabinofuranoside (6b). A solution of 5b (141 mg, 0.22 mmol), 2 (97.5 mg, 0.20 mmol), and triphenylcarbenium tetrafluoroborate (6.6 mg, 0.02 mmol) in methylene chloride (1.4 mL) was kept at 45 °C for 80 min. The reaction was terminated by the addition of pyridine (0.5 mL) and methanol (1.0 mL), and the solution was diluted with chloroform (20 mL). The chloroform solution was washed with water, dried (Na_2SO_4), and evaporated to a syrup, which was chromatographed with hexane-ethyl acetate

(6:1 v/v) to give 6b (51 mg, 33%); NMR δ 5.28 (s, 1 H, H-1), 5.46 (s, 1 H, H-1'), 5.56 (d, 1 H, J 0.9 Hz, H-2), 5.64 (s, 1 H, H-2').

Benzyl 5-O-(α-D-arabinofuranosyl)-α-D-arabinofuranoside (7a). A 5% methanolic solution of sodium methoxide (1 mL) was added to the solution of 6a (1.0 g) in chloroform (5 mL)-methanol (5 mL) mixture. The resulting mixture was kept at room temperature for 15 min and neutralized with Dowex 50 (H^+) in water. After filtration, the filtrate was diluted with chloroform and water. The aqueous layer was separated from the organic one, washed with chloroform, and concentrated to dryness to give a dimeric free glycoside 7a (392 mg, 94 %); NMR δ 3.71 (dd, 1 H, J 5.8 and 12.2 Hz, H-5a'), 3.78 (dd, 1 H, J 3.4 and 11.6 Hz, H-5b), 3.82 (dd, 1 H, J 3.4 and 12.2 Hz, H-5b'), 3.88 (dd, 1 H, J 5.8 and 11.6 Hz, H-5a), 3.95 (dd, 1 H, J 3.4 and 6.1 Hz, H-3'), 4.00 (dd, 1 H, J 3.4 and 6.1 Hz, H-3), 5.07 (d, 1 H, J 1.5 Hz, H-1'), 5.11 (d, 1 H, J 1.8 Hz, H-1), 7.39-7.45 (m, 5 H, 1 Ph).

Allyl 5-O-α-D-arabinofuranosyl)-α-D-arabinofuranoside (7b). A 5% methanolic solution of sodium methoxide (2 mL) was added to the solution of 6b (1.0 g) in chloroform (6 mL)-methanol (20 mL) mixture. The resulting mixture was kept at room temperature for 30 min and neutralized with Dowex 50 (H^+) in water. After filtration, the filtrate was diluted with chloroform and water. The aqueous layer was separated from the organic one, washed with chloroform, and evaporated to dryness to give a dimeric free glycoside 7b (370 mg, 89%); NMR δ 3.70 (dd, 1 H, J 6.0 and 12.4 Hz, H-5a'), 3.78 (dd, 1 H, J 3.2 and 11.5 Hz, H-5b), 3.82 (dd, 1 H, J 3.4 and 12.4 Hz, H-5b'), 3.87 (dd, 1 H, J 5.7 and 11.5 Hz, H-5a), 3.94 (ddd, 1 H, J 0.6, 3.1, and 5.8 Hz, H-3'), 4.01 (ddd, 1 H, J 0.6, 3.4, and 6.1 Hz, H-3), 5.06-5.07 (2 H, H-1 and H-1').

Attempt to remove the benzyl or the allyl group from 7a,b and checking the products by HPLC. A solution of 7a (392 mg) in water (50 mL) was hydrogenated in the presence of 10% Pd/C (400 mg) for 7 h and filtered. The filtrate was concentrated to dryness and the residual product was analyzed by HPLC. Compound 7b (171

mg) also was treated with acetic acid (1 mL), sodium acetate (168 mg), palladium chloride (160 mg), and water (0.05 mL) at room temperature for 22 h and filtrated. HPLC was performed at 60 °C using acetonitrile-water (70:30 v/v) as eluent. The sample derived from 7a revealed a single peak of a retention time different from arabinose; whereas the sample from 7b showed one large peak and two small ons. The retention time of the major peak was identical with that of authentic arabinose.

Benzyl 5-O-(2,3-di-O-benzoyl-5-O-triphenylmethyl-α-D-arabinofuranosyl)-2,3-di-O-benzoyl-α-D-arabinofuranoside (8). To a solution of dimeric free glycoside 7a (1.20 g, 3.23 mmol) in dried pyridine (12 mL) was added triphenylmethyl chloride (1.08 g, 3.87 mmol). The mixture was kept at room temperature for 3 days and diluted with benzene and water. The organic layer was separated, dried ($MgSO_4$), and concentrated to a syrup, which was chromatographed with chloroform-methanol (9:1 v/v) to give syrupy 8 (1.85 g, 56%); $[\alpha]_D^{25}$ +8.3° (c 1.12, $CHCl_3$), NMR δ 5.33 (s, 1 H, H-1), 5.40 (s, 1 H, H-1'), 7.15-8.04 (m, 40 H, 8 Ph).

Anal. Calcd for $C_{64}H_{54}O_{13}$: C, 74.55; H, 5.28. Found: C, 74.68; H, 5.30.

Benzyl O-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside heptabenzoate (9). A solution of 8 (1.85 g, 1.79 mmol), 2 (0.875 g, 1.79 mmol), and triphenylcarbenium tetrafluoroborate (119 mg, 0.36 mmol) in methylene chloride (10 mL) was kept at 0 °C for 30 h. The reaction was terminated by the addition of pyridine (5 mL) and methanol (10 mL), and the solution was diluted with chloroform. The chloroform solution was washed with water, dried (Na_2SO_4), and concentrated to a syrup, which was chromatographed with hexane-ethyl acetate (6:1 v/v) to give 9 (940 mg, 35%); $[\alpha]_D^{25}$ +11.3° (c 0.29, $CHCl_3$), NMR δ 5.32 (s, 1 H, H-1), 5.40 (s, 1 H, H-1'), 5.47 (s, 1 H, H-1"), 7.14-8.03 (m, 40 H, 8 Ph).

Anal. Calcd for $C_{71}H_{60}O_{20}$: C, 69.15; H, 4.90. Found: C, 69.78; H, 4.99.

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