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Note

The synthesis of tetra-, penta-, and hexa-saccharides related to an L-arabino-D-glucan*

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We have previously reported an investigation of the structure of the water-soluble polysaccharide that was isolated from the bark of *Melia azadirachta* (Meliaceae)[1,2]. GIa is a GIa(1→4)-α-D-glucan having one (1→6)-α-L-arabinofuranosyl group for every five D-glucose residues (**1**). GIa showed a strong antitumor effect against Sarcoma-180. In our previous paper[3], we reported the synthesis of the trisaccharides, methyl 6-*O*-α-L-arabinofuranosyl-4-*O*-α-D-glucopyranosyl-β-D-glucopyranoside and methyl *O*-α-L-arabinofuranosyl-(1→6)-*O*-α-D-glucopyranosyl-(1→4)-β-D-glucopyranoside, related to an L-arabino-D-glucan. We report herein the synthesis, as model compounds, of tetra-, penta-, and hexa-saccharides that contain the basic structural features of the L-arabino-D-glucan.

The synthesis of tetrasaccharide **7**, which corresponds to the partial structure unit of GIa (**1**), was started by condensation of methyl 2,3,6,2′,3′,6′,2″,3″-octa-*O*-acetyl-β-D-maltotrioside (**4**) [which had been prepared from methyl 2,3,6,2′,3′,6′,2″,3″-octa-*O*-acetyl-4″,6″-*O*-benzylidene-β-D-maltotrioside (**3**)] with 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl bromide[4,5] (**5**) to give the α-L-linked tetrasaccharide, methyl 2,3,6-2′,3′,6′,2″,3″-octa-*O*-acetyl-6″-*O*-(2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl)-β-D-maltotrioside (**6**) in 53% yield. Its ^{1}H-n.m.r. spectrum showed signals characteristic for three benzoyl, one methoxyl, and eight acetyl groups. Compound **6** was *O*-deacylated with triethylamine to give methyl 6″-*O*-α-L-arabinofuranosyl-β-D-maltotrioside (**7**), the ^{1}H-n.m.r. spectrum of which indicated four H-1 signals at δ 4.34 (d, *J* 8 Hz, H-1), 5.00 (s, H-1‴), and 5.34 (d, *J* 4 Hz, H-1′,1″), and the ^{13}C-n.m.r. spectrum four anomeric carbon atoms. Introduction of the α-L-arabinofuranosyl group at O-6 deshielded C-6″ by 5.9 p.p.m., as

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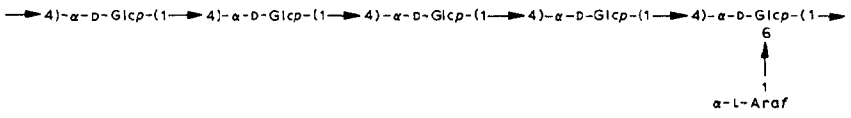

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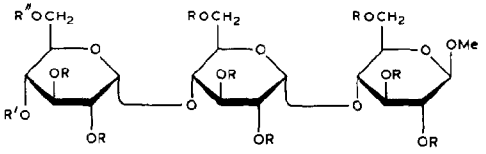
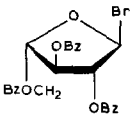


2 R = R′ = H
3 R = Ac; R′, R″ = CHPh
4 R = Ac; R′, R″ = H



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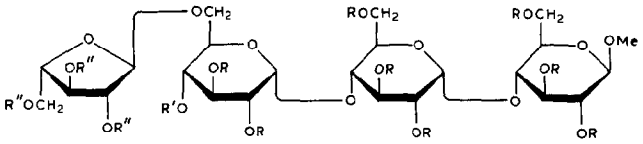
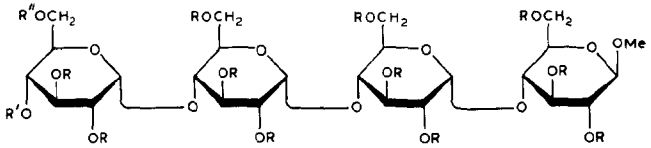
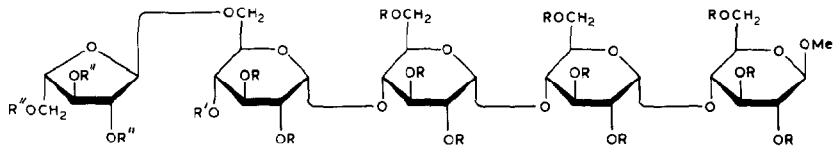


6 R = Ac, R′ = H, R″ = Bz
7 R = R′ = R″ = H



8 R = R′ = R″ = H
9 R = Ac; R′, R″ = CHC_6H_5
10 R = Ac, R′, R″ = H



11 R = Ac, R′ = H, R″ = Bz
12 R = R′ = R″ = H

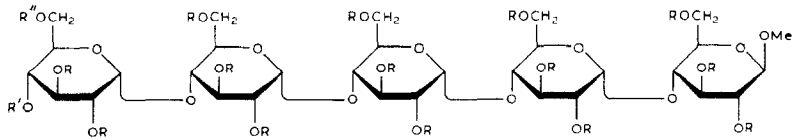
compared with methyl β-D-glucopyranoside[6] (δ 61.9). The α-L configuration for the newly formed glycosidic bond in **7** was evident from the ^{13}C-n.m.r. spectrum (C-1‴ at δ 109.0)[3,6]. The ^{13}C-shifts of the tetrasaccharide derivatives and related compounds are listed in Table I.

TABLE I

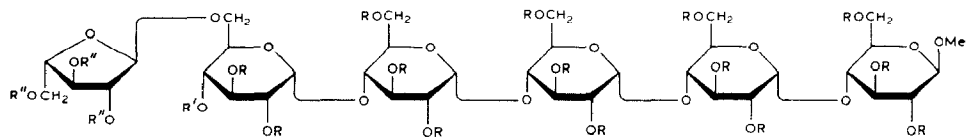
^{13}C-N.M.R. DATA (δ) FOR MALTOTRIOSE DERIVATIVES **2–4, 6** AND **7**[a]

Carbon atom	*Compound*				
	2	**3**	**4**	**6**	**7**
C-1	104.2	101.0	101.1	101.1	104.2
C-2	74.4	71.8	71.8	71.7	74.3
C-3	77.3	72.2	72.5	72.2	77.3
C-4	78.1	75.4	75.3	75.3	78.6
C-5	75.6	69.0	69.6	72.1	75.6
C-6	61.8	62.8	63.2	63.1	61.8
C-1′	100.6	95.7	95.6	95.6	100.6
C-2′	74.0	70.5	70.4	70.6	72.5
C-3′	72.6	72.1	72.0	72.2	74.1
C-4′	77.9	73.7	73.5	73.6	78.2
C-5′	72.3	68.5	68.4	70.3	72.3
C-6′	61.6	62.2	62.0	62.8	61.6
C-1″	100.9	96.5	96.0	95.8	101.0
C-2″	72.9	70.9	71.3	72.1	72.8
C-3″	74.0	72.6	72.8	72.2	74.1
C-4″	70.5	78.8	68.1	68.1	70.6
C-5″	73.8	63.7	69.2	69.2	74.0
C-6″	61.6	68.5	62.6	66.3	67.8
OCH_3	58.3	56.9	57.0	56.9	58.3
C_6H_5CH		101.7			
C-1‴				106.5	109.0
C-2‴				80.8	82.2
C-3‴				77.6	77.5
C-4‴				82.4	84.7
C-5‴				63.7	62.2

[a]For solutions of compound **3, 4**, and **6** in $CDCl_3$, and for solutions of **2** and **7** in D_2O.



13 R = R′ = R″ = H
14 R = Ac, R′, R″ = CHC_6H_5
15 R = Ac, R′ = R″ = H



16 R = Ac, R′ = H, R″ = Bz
17 R = R′ = R″ = H

TABLE II

^{13}C-N.M.R. DATA (δ) FOR MALTOTETRAOSE DERIVATIVES **8–12**[a]

Carbon atom	*Compound*				
	8	**9**	**10**	**11**	**12**
C-1	104.2	101.0	101.0	101.0	104.2
C-2	74.4	71.9	71.6	71.9	74.4
C-3	77.3	72.2	72.0	72.2	77.3
C-4	78.1	75.4	75.4	75.4	78.6
C-5	75.6	70.4	69.1	71.5	75.6
C-6	61.8	62.9	62.9	63.1	61.7
C-1′	100.6	95.8	95.8	95.7	100.6
C-2′	74.1	71.6	70.5	71.9	74.4
C-3′	72.6	72.2	72.0	72.2	72.7
C-4′	78.1	73.8	73.9	73.9	78.2
C-5′	72.6	69.0	69.1	70.5	72.6
C-6′	61.6	62.4	62.9	62.6	61.6
C-1″	100.8	95.8	95.8	95.7	100.8
C-2″	74.4	70.9	70.5	71.8	74.4
C-3″	72.6	72.1	72.0	72.1	72.7
C-4″	78.0	73.4	73.6	73.5	77.5
C-5″	72.3	69.0	69.1	70.5	72.3
C-6″	61.6	62.1	61.7	62.6	61.5
C-1‴	100.8	96.4	95.8	95.7	101.0
C-2‴	72.9	71.9	71.6	71.8	72.8
C-3‴	74.1	72.1	72.0	72.1	74.1
C-4‴	70.5	78.8	69.1	69.0	70.5
C-5‴	73.9	63.7	69.1	69.2	74.0
C-6‴	61.6	68.4	62.4	66.1	67.8
C-1⁗				106.5	109.0
C-2⁗				80.1	82.2
C-3⁗				77.6	78.1
C-4⁗				82.4	84.7
C-5⁗				63.7	62.2
OCH_3	58.3	56.9	56.9	56.9	58.3
C_6H_5CH		101.6			

[a]For solutions of compound **9**, **10**, and **11** in $CDCl_3$, and for solutions of **8** and **12** in D_2O.

Similarly, methyl 2,3,6,2′,3′,6′,2″,3″,6″,2‴,3‴-undeca-*O*-acetyl-β-D-maltotetraoside (**10**) (which was prepared from the 4‴,6‴-*O*-benzylidene compound **9**) and bromide **5** in nitromethane containing mercuric cyanide gave, after column chromatography, in 29% yield (based on **10**), a pentasaccharide containing a (1→6)-linked α-L-arabinofuranosyl group, methyl 2,3,6,2′,3′,6′,2″,3″,6″,2‴,3‴-undeca-*O*-acetyl-6‴-*O*-(2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl)-β-D-maltotetraoside (**11**). Removal of the blocking groups with 50% methanolic tri-

TABLE III

^{13}C-N.M.R. DATA (δ) FOR MALTOPENTAOSE DERIVATIVES **13–17**[a]

Carbon atom	*Compound*				
	13	**14**	**15**	**16**	**17**
C-1	104.2	101.1	101.1	101.3	104.2
C-2	74.5	71.9	71.6	71.8	74.4
C-3	77.3	72.1	72.1	72.4	77.3
C-4	78.1	75.4	75.6	75.2	78.5
C-5	75.6	70.5	69.0	71.7	75.6
C-6	61.6	62.9	62.9	62.9	61.8
C-1′	100.8	95.8	95.6	95.7	100.6
C-2′	72.7	71.7	70.5	71.8	72.7
C-3′	74.5	72.1	72.1	72.1	74.4
C-4′	78.1	73.8	73.7	73.8	78.3
C-5′	72.3	70.5	69.0	70.5	72.3
C-6′	61.6	62.6	62.8	62.6	61.5
C-1″	100.8	95.8	95.6	95.7	100.8
C-2″	72.7	70.9	70.5	71.7	72.7
C-3″	74.5	72.1	72.1	72.1	74.4
C-4″	78.1	73.5	73.1	73.6	78.0
C-5″	72.3	69.1	69.0	70.5	72.3
C-6″	61.6	62.2	62.7	62.5	61.5
C-1‴	100.9	95.8	95.8	95.8	100.8
C-2‴	72.7	71.7	70.5	71.7	72.7
C-3‴	74.1	72.1	72.3	72.1	74.1
C-4‴	78.1	73.2	72.7	73.2	77.5
C-5‴	72.3	69.1	69.0	70.5	72.3
C-6‴	61.6	62.0	62.4	62.1	61.3
C-1⁗	100.9	96.4	95.8	95.8	101.0
C-2⁗	72.9	71.9	71.8	71.7	72.9
C-3⁗	74.1	72.1	72.3	72.4	74.1
C-4⁗	70.5	78.9	69.2	69.0	70.5
C-5⁗	73.8	63.7	70.1	69.2	74.0
C-6⁗	61.6	68.5	62.3	66.3	67.8
C-1⁗′				105.7	109.0
C-2⁗′				80.3	82.2
C-3⁗′				77.6	78.0
C-4⁗′				82.6	84.7
C-5⁗′				63.7	62.2
OCH_3	58.3	56.9	56.9	56.9	58.3
C_6H_5CH		101.7			

[a]For solutions of compound **14, 15**, and **16** in $CDCl_3$, and for solutions of **13** and **17** in D_2O.

ethylamine afforded methyl 6‴-*O*-α-L-arabinofuranosyl-β-D-maltotetraoside (**12**). The α-L configuration for the newly formed glycosidic bond in **12** was evident from the ^{13}C-n.m.r. spectrum (C-1‴ at δ 109.0) (Table II).

The hexasaccharide, methyl 6⁗-*O*-α-L-arabinofuranosyl-β-D-maltopentaoside (**17**) was synthesized by conversion of methyl β-D-maltopentaoside (**13**) into the benzylidene derivative **14** by the method of Evans[7] using α,α-dimethoxytoluene. In all cases of preparation of the acetylated benzylidene derivatives (**3**, **9**, and **14**), the yields were very low. This may be due to the insolubility of methyl maltooligosaccharide and because the acetylation was performed on the reaction mixture, *i.e.*, without an intermediate workup. Condensation of **15**, obtained by removal of the benzylidene group of **14**, with bromide **5** in the presence of mercuric cyanide and molecular sieves, gave the hexasaccharide derivative **16** in 52% yield. *O*-Deacetylation and *O*-debenzoylation of **16** at room temperature with triethylamine in 50% methanol gave methyl 6⁗-*O*-α-L-arabinofuranosyl-β-D-maltopentaoside (**17**). The ^{13}C-n.m.r. spectrum of **17** in D_2O contained signals for C-1,C-1′,C1″,C-1‴,C-1⁗, and C-1⁗′ at δ 104.2, 100.6, 100.8, 100.8, 101.0, and 109.0, respectively. The introduction of the α-L-arabinofuranosyl residue at OH-6⁗ in **13** was confirmed by a 6.2 p.p.m. downfield shift of the C-6⁗ signal of **17** (from δ 61.6 in **13** to 67.8), as shown in Table III. No anomeric impurities were observed by ^{1}H- and ^{13}C-n.m.r. spectrometry in all the compounds described.

EXPERIMENTAL

General methods. — Melting points were determined with a Yanagimoto microapparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 digital polarimeter. ^{1}H-N.m.r. spectra were recorded with a JNM MH-100 spectrometer, and ^{13}C-n.m.r. spectra with a FX-100 instrument, tetramethylsilane being the internal standard in both cases. T.l.c. was conducted on precoated silica gel plates (Merck GF-254), and the detection of compounds was achieved by quenching of u.v. fluorescence and with 10% H_2SO_4 solution. Column chromatography was carried out on silica gel (Merck Kieselgel 60).

Methyl β-D-maltotrioside (**2**), *methyl β-D-maltotetraoside* (**8**), *and methyl β-D-maltopentaoside* (**13**). — A maltooligosaccharide mixture (30 g), purchased from Pfanstiehl laboratories, was acetylated with acetic anhydride (70 mL) and pyridine (70 mL). A solution of the glycosyl bromides (46 g) was prepared from the mixture of acetates (50 g) by treatment with 25% HBr–acetic acid (90 mL) in chloroform (110 mL), and then methanol (200 mL) and mercuric cyanide (20 g) were added. The mixture was stirred for 6 h at 40°, and filtered, and the filtrate concentrated to dryness. The residue (52.4 g) of the mixture of methyl β-D-maltooligosaccharide acetates was chromatographed on silica gel in 4:1 benzene–acetone to provide the pure acetates of methyl trioside (9.4 g), tetraoside (5.7 g), and pentaoside (7.2 g). Compound **2** (4.5 g), **8** (3 g), and **13** (4 g) were prepared by deacetylation with triethylamine (8 mL) in 50% methanolic solution (30 mL) of the corresponding acetate.

Methyl 2,3,6,2′,3′,6′,2″,3″-octa-O-acetyl-4″,6″-O-benzylidene-β-D-maltotrioside (**3**). — To a solution of methyl β-D-maltotrioside (**2**; 3 g, 5.8 mmol) in benzaldehyde (8 mL) was added anhydrous $ZnCl_2$ (5 g). The mixture was stirred overnight at room temperature, and then acetylated with pyridine (12 mL) and acetic anhydride (5 mL), and the solution was kept overnight. The mixture was poured into ice–water. The precipitate was washed with petroleum ether and chromatographed on a column of silica gel. The product, eluted with 4:1 (v/v) benzene–acetone, crystallized from methanol (500 mg, 12.0%), m.p. 98–99°, $[\alpha]_D^{21}$ +56.6° (*c* 13.5, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.56–7.26 (m, 5 H, C_6H_5CH), 5.46 (s, 1 H, C_6H_5CH), 3.45 (s, 3 H, OCH_3), and 2.12–1.95 (24 H, 8 $COCH_3$).

Anal. Calc. for $C_{42}H_{54}O_{24} \cdot H_2O$: C, 52.50; H, 5.87. Found: C, 52.26; H, 5.76.

Methyl 2,3,6,2′,3′,6′,2″,3″-octa-O-acetyl-β-D-maltotrioside (**4**). — A solution of **3** (130 mg, 0.14 mmol) in 60% acetic acid (5 mL) was stirred for 4 h at 40°. It was then poured into ice–water and extracted with chloroform, and the extract washed with water, dried (Na_2SO_4), and evaporated under diminished pressure to give a solid (87 mg, 74%), m.p. 66–68°, $[\alpha]_D^{21}$ +42.5° (*c* 3.74, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 3.46 (s, 3 H, OCH_3) and 2.14–1.97 (24 H, 8 $COCH_3$).

Anal. Calc. for $C_{35}H_{50}O_{24}$: C, 49.18; H, 5.90. Found: C, 49.47; H, 5.95.

Methyl 2,3,6,2′,3′,6′,2″,3″-octa-O-acetyl-6″-O-(2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl)-β-D-maltotrioside (**6**). — A solution of 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl bromide (**5**) (308.7 mg, 0.59 mmol) in nitromethane (3 mL) was added to a mixture of **4** (87 mg, 0.1 mmol), $Hg(CN)_2$ (1 g), and molecular sieve 4A (0.3 mg) in the same solvent (3 mL). After being stirred for 3 h at 60°, the mixture was cooled and washed successively with saturated aqueous $NaHCO_3$, saturated aqueous NaCl, and water, dried (Na_2SO_4), and evaporated to give a syrup that contained, as shown by t.l.c. in 4:1 (v/v) benzene–acetone, a major product (R_F 0.46). The residue was chromatographed on a column of silica gel. The product, eluted with 4:1 (v/v) benzene–acetone, crystallized from ethanol (70 mg, 53.0%), m.p. 82–84°, $[\alpha]_D^{20}$ +47.5° (*c* 2.8, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.16–7.95 (m, 6 H, arom.), 7.60–7.24 (m, 9 H arom.), and 2.12–1.92 (24 H, 8 $COCH_3$).

Anal. Calc. for $C_{61}H_{70}O_{31}$: C, 56.42; H, 5.43. Found: C, 56.83; H, 5.74.

Methyl 6″-O-α-L-arabinofuranosyl-β-D-maltotrioside (**7**). — Compound **6** (50 mg, 0.039 mmol) was *O*-deacylated with triethylamine (0.5 mL) in 50% aqueous methanol (4 mL). The mixture was kept overnight at room temperature, and then evaporated *in vacuo* to give a white powder (25 mg, 98%), $[\alpha]_D^{21}$ +45° (*c* 0.78, water); t.l.c. (13:7:2, lower phase, v/v, chloroform–methanol–water) R_F 0.11; ^{1}H-n.m.r. (D_2O): δ 5.34 (d, *J* 4 Hz, H-1′,1″), 5.00 (s, H-1‴), 4.34 (d, *J* 8 Hz, H-1), and 3.53 (3 H, OCH_3).

Anal. Calc. for $C_{24}H_{42}O_{20}$: C, 44.34; H, 6.51. Found: C, 44.62; H, 6.71.

Methyl 2,3,6,2′,3′,6′,2″,3″,6″,2‴,3‴-undeca-O-acetyl-4‴,6‴-O-benzylidene-β-D-maltotetraoside (**9**). — To a solution of methyl β-D-maltotetraoside (**8**; 2 g, 2.94 mmol) in benzaldehyde (5 mL) was added anhydrous $ZnCl_2$ (3 g). The mixture was stirred overnight, and then acetylated with pyridine (5 mL) and acetic anhydride (4

mL), and the solution was kept overnight. After a work-up similar to that described for the preparation of **3**, compound **9** crystallized from methanol (299 mg, 8.3%), m.p. 115–116°, $[\alpha]_D^{18}$ +83° (*c* 3.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.60–7.20 (m, 5 H, CHC_6H_5), 5.44 (s, 1 H, CHC_6H_5), 3.46 (s, 3 H, CH_3) and 2.16–1.96 (33 H, 11 $COCH_3$).

Anal. Calc. for $C_{54}H_{70}O_{32}$: C, 52.68; H, 5.73. Found: C, 52.01; H, 5.33.

*Methyl 2,3,6,2′,3′,6′,2″,3″,6″,2‴,3‴-undeca-*O*-acetyl-β-*D*-maltotetraoside* (**10**). — A solution of **9** (215 mg, 0.17 mmol) in 60% acetic acid (10 mL) was stirred for 4 h at 40° and worked up in a manner similar to that described for the preparation of **4** to give a solid (128.9 mg, 64.5%), m.p. 108–109°, $[\alpha]_D^{18}$ +95° (*c* 0.61, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 3.48 (s, 3 H, OCH_3) and 2.16–2.01 (33 H, 11 $COCH_3$).

Anal. Calc. for $C_{47}H_{66}O_{32}$: C, 49.39; H, 5.82. Found: C, 49.46; H, 5.52.

*Methyl 2,3,6,2′,3′,6′,2″,3″,6″,2‴,3‴-undeca-*O*-acetyl-6‴-*O*-(2,3,5-tri-*O*-benzoyl-α-*L*-arabinofuranosyl)-β-*D*-maltotetraoside* (**11**). — A solution of 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl bromide (**5**; 157.5 mg, 0.3 mmol) in nitromethane (3 mL) was added to a mixture of **10** (128.9 mg, 0.11 mmol), $Hg(CN)_2$ (1 g), and molecular sieve 4A (0.3 g) in the same solvent (3 mL), as described for the preparation of **6**. The product, eluted with 4:1 (v/v) benzene–acetone, crystallized from ethanol (51.2 mg, 28.6%), m.p. 112–113°, $[\alpha]_D^{18}$ +85° (*c* 0.4, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.96–8.20 (m, 6 H, arom.), 7.19–7.66 (m, 9 H, arom.), 3.48 (s, 3 H, OCH_3) and 2.17–1.93 (33 H, 11 $COCH_3$).

Anal. Calc. for $C_{73}H_{86}O_{39}$: C, 55.23; H, 5.46. Found: C, 55.42; H, 5.61.

*Methyl 6‴-*O*-α-*L*-arabinofuranosyl-β-*D*-maltotetraoside* (**12**). — Compound **11** (50 mg, 0.03 mmol) was *O*-deacylated with triethylamine (0.5 mL) in 50% aqueous methanol (4 mL), overnight at room temperature. The solution was evaporated to give a white powder (25.0 mg, 97.7%), $[\alpha]_D^{21}$ +67° (*c* 1.4, water), t.l.c. (13:7:2, lower phase, v/v, chloroform–methanol–water) R_F 0.09; ^{1}H-n.m.r. (D_2O): δ 5.37 (d, *J* 3 Hz, H-1′,1″,1‴), 5.04 (s, H-1⁗), 4.38 (d, *J* 8 Hz, H-1), and 3.56 (3 H, OCH_3).

Anal. Calc. for $C_{30}H_{52}O_{25} \cdot H_2O$: C, 43.37; H, 6.55. Found: C, 43.25; H, 6.79.

*Methyl 2,3,6,2′,3′,6′,2″,3″,6″,2‴,3‴,6‴,2⁗,3⁗-tetradeca-*O*-acetyl-4⁗,6⁗-*O*-benzylidene-β-*D*-maltopentaoside* (**14**). — To a solution of methyl β-D-maltopentaoside (**13**; 1.81 g, 2.15 mmol) in *N*,*N*-dimethylformamide (30 mL) was added α,α-dimethoxytoluene (1.96 g) and *p*-toluenesulfonic acid (42 mg). The mixture was stirred overnight at room temperature, and then acetylated overnight with pyridine (15 mL) and acetic anhydride (15 mL). The mixture was poured into ice–water, the precipitate washed with petroleum ether, and then chromatographed on a column of silica gel. The product, eluted with 4:1 (v/v) benzene–acetone, crystallized from methanol (312 mg, 9.6%), m.p. 123–124°, $[\alpha]_D^{24}$ +84° (*c* 0.49, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.46–7.27 (m, 5 H, CHC_6H_5), 5.47 (s, 1 H, CHC_6H_5), 3.49 (s, 3 H, OCH_3), and 2.19–1.85 (42 H, 14 $COCH_3$).

Anal. Calc. for $C_{66}H_{86}O_{40}$: C, 52.17; H, 5.70. Found: C, 52.43; H, 5.81.

Methyl 2,3,6,2′,3′,6′,2″,3″,6″,2‴,3‴,6‴,2⁗,3⁗,6⁗-tetradeca-O-acetyl-β-D-maltopentaoside (**15**). — A solution of **14** (261 mg, 0.17 mmol) in 60% acetic acid (15 mL) was stirred for 4 h at 40°. The usual work-up gave a solid (81 mg, 32.9%), m.p. 119–121°, $[\alpha]_D^{22}$ +88° (*c* 0.47, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 3.49 (s, 3 H, OCH_3), and 2.19–1.98 (42 H, 14 $COCH_3$).

Anal. Calc. for $C_{59}H_{82}O_{40}$: C, 49.51; H, 5.77. Found: C, 49.67; H, 5.93.

Methyl 2,3,6,2′,3′,6′,2″,3″,6″,2‴,3‴,6‴,2⁗,3⁗,6⁗-tetradeca-O-acetyl-6⁗-O-(2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl)-β-D-maltopentaoside (**16**). — A solution of the bromide **5** (308 mg, 0.59 mmol) in nitromethane (10 mL) was added to a mixture of **15** (54 mg, 0.04 mmol), $Hg(CN)_2$ (782 mg), and molecular sieve 4A (304 mg) in the same solvent (3 mL). In coupling the donor to acceptor, the same conditions were used as those described for the preparation of **6**. The product was eluted with 4:1 (v/v) benzene–acetone and crystallized from ethanol (46 mg, 52%), m.p. 110–111°, $[\alpha]_D^{20}$ +126° (*c* 0.14, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.14–7.90 (m, 6 H, arom.), 7.74–7.20 (m, 9 H, arom.), 3.49 (s, 3 H, OCH_3) and 2.19–1.98 (42 H, 14 $COCH_3$).

Anal. Calc. for $C_{85}H_{102}O_{47}$: C, 54.43; H, 5.48. Found: C, 54.02; H, 5.47.

Methyl 6⁗-O-α-L-arabinofuranosyl-β-D-maltopentaoside (**17**). — Compound **16** (33 mg, 0.02 mmol) was *O*-deacylated with triethylamine (1 mL) in 50% aqueous methanol (4 mL), and the solution evaporated to give a white powder (17 mg, 97%), m.p. 120–123°, $[\alpha]_D^{20}$ +80° (*c* 0.23, water); ^{1}H-n.m.r. (D_2O): δ 5.37 (d, *J* 4 Hz, H-1′,1″,1‴,1⁗), 5.04 (s, H-1⁗), and 4.36 (d, *J* 8 Hz, H-1).

Anal. Calc. for $C_{36}H_{62}O_{30} \cdot 3\ H_2O$: C, 42.02; H, 6.66. Found: C, 41.52; H, 6.21.

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REFERENCES

1 T. Fujiwara, T. Takeda, Y. Ogihara, M. Shimizu, T. Nomura, and Y. Tomita, *Chem. Pharm. Bull.*, 30 (1982) 4025–4030.
2 T. Fujiwara, T. Takeda, Y. Ogihara, M. Shimizu, T. Nomura, and Y. Tomita, *Chem. Pharm. Bull.*, 32 (1984) 1385–1391.
3 T. Fujiwara, T. Takeda, and Y. Ogihara, *Carbohydr. Res.*, 141 (1985) 168–171.
4 H. G. Fletcher, Jr., *Methods Carbohydr. Chem.*, 2 (1963) 228–230.
5 J. Hirsch, E. Petrakova, and J. Schraml, *Carbohydr. Res.*, 131 (1984) 219–226.
6 P. A. J. Gorin and M. Mazurek, *Can. J. Chem.*, 53 (1975) 1212–1223.
7 M. E. Evans, *Methods Carbohydr. Chem.*, 8 (1980) 313–315.