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Synthesis of the α-L-Ara*f*-(1→2)-β-D-Gal*p*-(1→6)-β-D-Gal*p*-(1→6)-[α-L-Ara*f*-(1→2)]-β-D-Gal*p*-(1→6)-D-Gal hexasaccharide as a possible repeating unit of the cell-cultured exudates of *Echinacea purpurea* arabinogalactan

Magdolna Csávás,[a] Anikó Borbás,[a] Lóránt Jánossy,[b] Gyula Batta,[c] András Lipták[a,b,*]

[a]*Research Group for Carbohydrates of the Hungarian Academy of Sciences, PO Box 70, H-4010 Debrecen, Hungary*

[b]*Department of Biochemistry, Faculty of Sciences, University of Debrecen, PO Box 55, H-4010 Debrecen, Hungary*

[c]*Research Group of Antibiotics of the Hungarian Academy of Sciences, PO Box 70, H-4010 Debrecen, Hungary*

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Dedicated to Professor Joachim Thiem on the occasion of his 60th birthday

Abstract

For the characterization of the supposed epitope of an arabinogalactan, isolated from the extract of the cell-cultured *Echinacea purpurea*, the title hexasaccharide was synthesized. The whole synthetic route was based on the 6-*O*-(methoxydimethyl)methyl ether (MIP) protecting group strategy. 2-*O*-Benzyl-3,4-*O*-isopropylidene-6-*O*-(methoxydimethyl)methyl-β-D-galactopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose was used to prepare the desired glycosyl donor and glycosyl acceptor both carrying a persistent *O*-benzyl group at position 2′. Reaction of the digalactose donor and the digalactose acceptor resulted in a β-(1→6)-linked galactose-containing tetrasaccharide in which OH-2′ and OH-2‴ were substituted with benzyl groups. Hydrogenolytic removal of the benzyl groups of the tetragalactose compound gave the diol aglycon which was diarabinosylated in one step to furnish the protected target compound, whose deprotection led to the title hexasaccharide. All of the synthesized compounds were characterized by ^{1}H and ^{13}C NMR spectra, as well as by MALDI-TOF mass-spectrometry measurements.

Keywords: *Echinacea purpurea*; Arabinogalactans; MIP ethers; Branched-hexasaccharide

1. Introduction

Among the plant tissue glycoproteins the arabinogalactan-proteins are the most widely distributed representatives in nature. Their biological functions are unknown, although the maple syrup of *Acer pseudoplatanus*,[1] the roots of *Angelica acutiloba* and *Bupleurum falcatum* are applied in folk-medicine for curing different diseases.[2,3] Similarly, the extract of the cell-cultured *Echinacea purpurea*[4,5] shows promising biological activity, and all of

* Corresponding author. Tel.: +36-52-512900x2256; fax: +36-52-512913.

E-mail address: liptaka@tigris.kltelhu (A. Lipták).

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these effects are attributed to the arabinogalactan components of the extracts. The exact structure of these polysaccharides are unknown, although monoclonal antibodies directed against epitopes of the polysaccharides can provide useful and fast structural information. In all of the above cases a β-(1→6)-linked galactan skeleton was anticipated to be present, and each third or fourth galactopyranoside unit was thought to be α-L-arabinofuranosylated at C-2. To obtain structurally well defined epitopes for further characterization of the monoclonal antibodies, three groups of researchers synthesized the following model oligosaccharides: α-L-Ara*f*-(1→2)-β-D-Gal*p*-(1→6)-β-D-Gal*p*-(1→6)-β-D-Gal*p*-(1→OMCUD),[6] β-D-Gal*p*-(1→6)-[α-L-Ara*f*-(1→2)]-β-D-Gal*p*-(1→6)-β-D-Gal*p*-(1→OMCUD),[6] β-D-Gal*p*-(1→6)-β-D-Gal*p*-(1→6)-[α-L-Ara*f*-(1→2)]-β-D-Gal*p*-(1→OMCUD),[6] β-D-Gal*p*-(1→6)-β-D-Gal*p*-(1→6)-[α-L-Ara*f*-(1→2)]-β-D-Gal*p*-(1→ODD),[7] α-L-Ara*f*-(1→2)-β-D-Gal*p*-(1→6)-D-Gal,[8] α-L-Ara*f*-(1→6)-β-D-Gal*p*-(1→6)-D-Gal,[8] (α-L-Ara*f*)$_2$-(1→2,6)-β-D-Gal*p*-(1→6)-D-Gal,[8] where MCUD and DD are 11-methoxycarbonylundecanyl and dodecyl spacers.

These target compounds are structurally very similar, but the synthetic approaches used are completely different.[6–8]

2. Results and discussion

Our synthetic goal was to prepare the hexasaccharide **1**, α-L-Ara*f*-(1→2)-β-D-Gal*p*-(1→6)-β-D-Gal*p*-(1→6)-[α-L-Ara*f*-(1→2)]-β-D-Gal*p*-(1→6)-D-Gal, which is the anticipated repeating unit and may be the epitope of the arabinogalactan isolated from the industrial scale cell culture of *E. purpurea*. Our key reaction was the treatment of a free β-D-galactopyranosyl unit with 2,2-dimethoxypropane in the presence of an acid catalyst to obtain 3,4-*O*-isopropylidene-6-*O*-(methoxydimethyl)methyl-β-D-galactopyranoside building blocks.[9] This reaction was developed in 1983,[8] and it was successfully employed for the preparation of the key disaccharide **2** starting either from galactopyranosyl-(1→6)-D-galactose or from β-D-galactopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose.[8] Compound **2** carries three persistent dioxolane-type blocking groups, one temporary 6′-*O*-(methoxydimethyl)methyl (MIP) function, and a free OH-2′ which is ready for further transformation. The only drawback of the application of compound **2** is that the MIP group is rather sensitive under the generally used glycosylation conditions, due to hydrolysis or its participation in condensation reactions.[8]

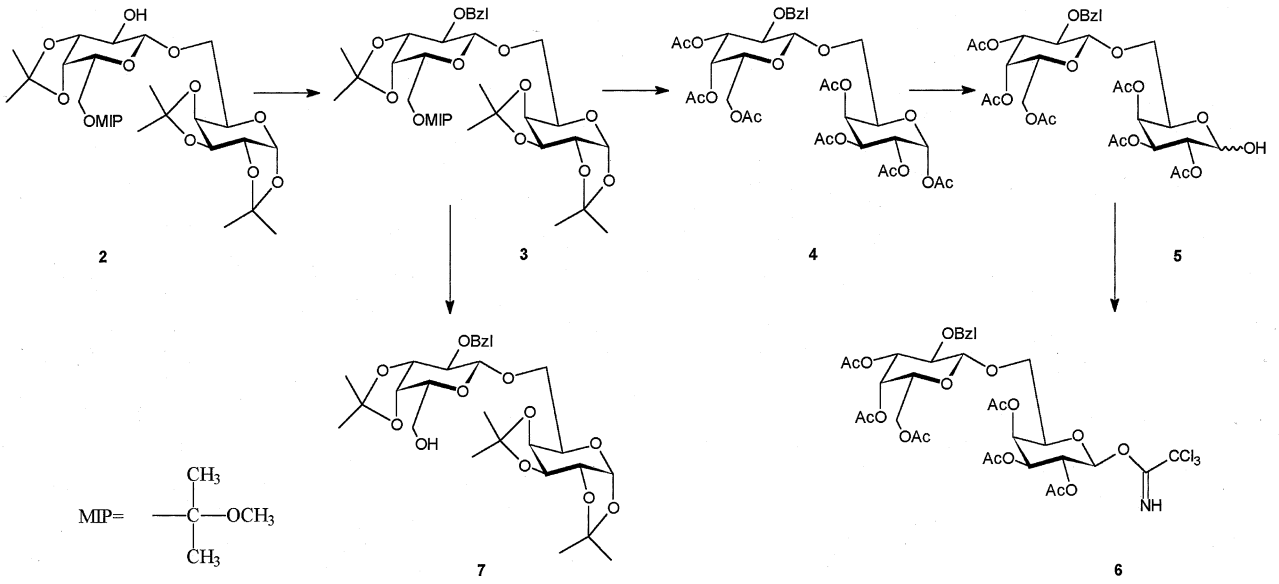
This difficulty was solved by avoiding the direct glycosylation of the MIP-protected disaccharide. Namely, our former synthetic strategy had been arabinosylation of compound **2** at position OH-2′, then, after splitting of the 6′-OMIP group, chain elongation of the β-(1→6)-galactan skeleton. Since our experiments showed either the sensitivity or reactivity of MIP-group under glycosylation conditions we have changed our strategy. First we elongated the galactan skeleton, and then formed the arabinosyl branches. For the preparation of building blocks, suitable for the synthesis of a tetragalactan chain, OH-2′ of compound **2** was benzylated to give **3**. The disaccharide **3** is useful for the preparation both of the glycosyl donor and the glycosyl acceptor in the synthesis of the target tetrasaccharide (**8**). Complete acid hydrolysis of the acetal groups of **3** resulted in a monobenzyl digalactoside, which was directly acetylated to obtain compound **4**[8] as an anomeric mixture (of pyranoses and furanoses) at the reducing end. The ratio of the four isomers (α-, β-pyranose and α-, β-furanose) was ~80:10:5:5.

The isolated pure 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-β-D-galactopyranosyl-(1→6)-1,2,3,4-tetra-*O*-acetyl-α-D-galactopyranose (**4**) was characterized by its ^{13}C NMR spectrum and selectively deacetylated at the anomeric position with hydrazine acetate to obtain the OH-1 compound (**5**) which was transformed without characterization into the β-trichloroacetimidoyl derivative (**6**) using K_2CO_3 as the base and trichloroacetonitrile as the reagent[10] and compound **3** was converted to glycosyl acceptor **7**[8] (Scheme 1).

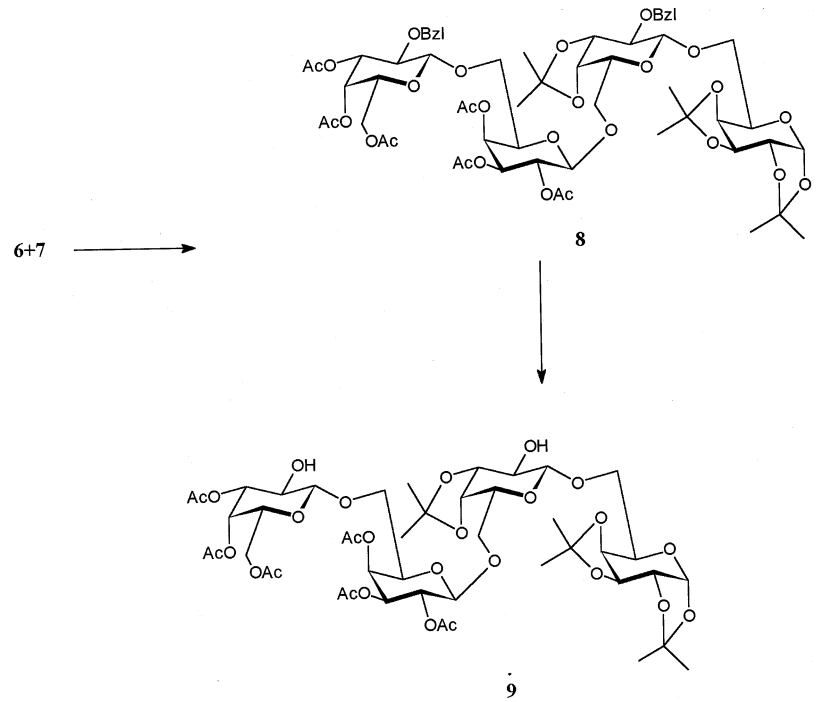
Trimethylsilyl triflate-promoted glycosylation of **7** with **6** proceeded with an excellent yield. The obtained tetrasaccharide (**8**) was

characterized by the NMR spectra and MALDI-TOF mass-spectrometry. Having the tetrasaccharide **8** in hand, the removal of the two benzyl groups was attempted. To avoid acetyl migration at the terminal galactopyranoside (OH-2‴) we used ethyl acetate as the solvent and Pd-on-carbon as the catalyst. These reaction conditions proved to be successful; after 14 h the reduction was complete and in compound **9** no acetyl migration could be detected either by chromatographic or by spectroscopic methods (Scheme 2).

The isolated diol **9** was used as the aglycone and glycosylation was achieved with the known 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl bromide (**10**)[11] in acetonitrile, in the



Scheme 1. Synthesis of the disaccharide-type glycosyl donor (**6**) and glycosyl acceptor (**7**) from the same building block (**3**).



Scheme 2. Synthesis of the tetrasaccharide diol (**9**) through compound **8**.

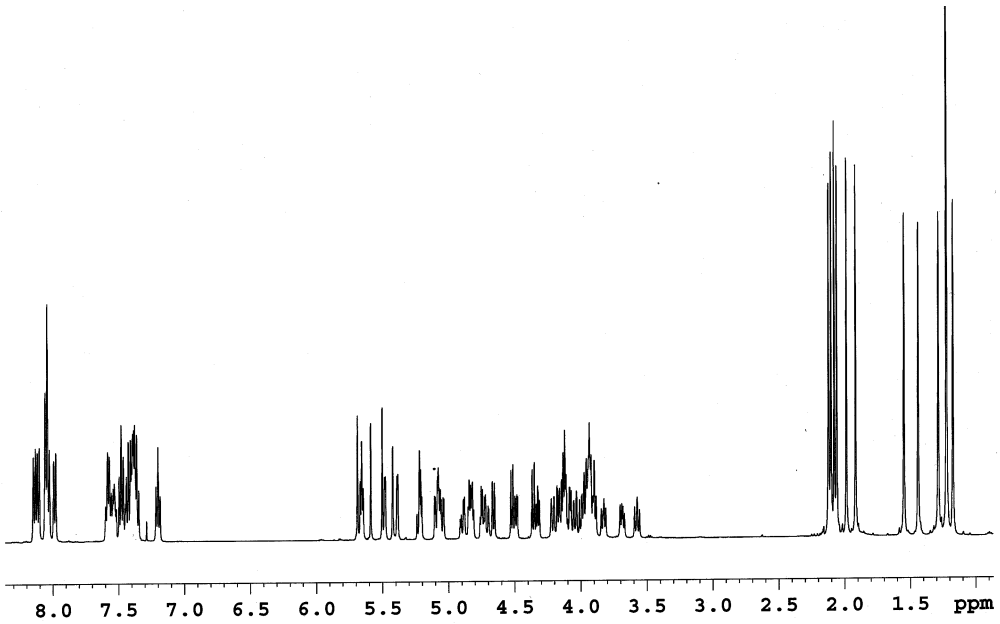
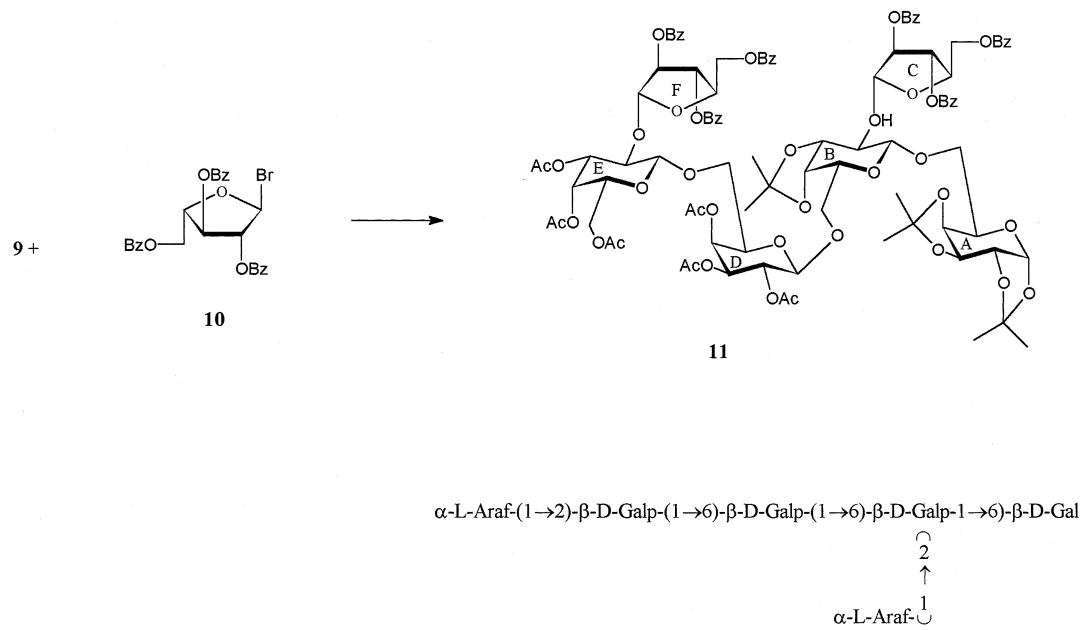


Fig. 1. 1D ^{1}H NMR spectrum of the fully protected hexasaccharide **11**. The spectrum was acquired at 320 K and 500 MHz in $CDCl_3$.



α-L-Araf-(1→2)-β-D-Galp-(1→6)-β-D-Galp-(1→6)-β-D-Galp-1→6)-β-D-Gal

2 ↑

α-L-Araf-1

Scheme 3. Structure of the fully protected hexasaccharide (**11**) and the free hexasaccharide (**1**).

presence of $Hg(CN)_2$ promoter to give the fully protected hexasaccharide (**11**). Compound **11** showed well-resolved ^{1}H and ^{13}C NMR spectra at 500 and 125 MHz (Fig. 1). The COSY, HETCOR and HMBC spectra allowed a complete assignment, and MALDI-TOF-MS also verified the hexasaccharide structure.

Deprotection of compound **11** required a strict sequence of reactions; first the isopropylidene groups were hydrolyzed with trifluoroacetic acid in dichloromethane in the presence of a very small amount of water, then the product was deacylated by Zemplén. Pure **1** was then obtained after chromatographic purification in a yield of 88% (Scheme 3).

The ^{1}H (Fig. 2) and ^{13}C NMR (Fig. 3) spectra of compound **1** were extremely overcrowded, and complete assignment could not be achieved even at 500 (125) MHz fields. Fortunately, the signals of the anomeric region of both spectra were quite well separated and complete assignment could be achieved in this region. Also, the $^{3}J_{H1,H2}$ and $^{1}J_{C1,H1}$ values were measured and these data unequivocally confirmed the declared structure of the hexasaccharide **1**, which was also substantiated by MALDI-TOF MS, using dihydroxybenzoic acid (DHB) as a matrix. The NMR data are collected in Tables 1 and 2.

3. Experimental

General methods.—Optical rotations were measured at rt with a Perkin–Elmer 241 automatic polarimeter. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. TLC was performed on Kieselgel 60 F_{254} (E. Merck) with detection by charring with 50% aq H_2SO_4. Column chromatography was performed on Silica Gel 60 (E. Merck, 0.062–0.200 nm). The organic solutions were dried over $MgSO_4$, and concentrated in a vacuum. The ^{1}H (200, 360 and 500 MHz) and ^{13}C NMR (50.3, 90.54, 125.76 MHz) spectra were recorded with Bruker WP-200SY, Bruker AM-360 and Bruker DRX-500 spectrometers in $CDCl_3$ or in D_2O solutions. Internal references: TMS (0.00 ppm for ^{1}H), $CDCl_3$ (77.00 ppm for ^{13}C).

MALDI-TOF MS analysis of the compounds was carried out in the positive reflectron mode using BIFLEX III mass spectrometer (Bruker, Germany) equipped with delayed-ion extraction. Spectra from multiple (at least 100) laser shots (N_2 laser, 337 nm) were summarized using 19 kV accelerating and 20 kV reflectron voltage. The compounds were identified as $[M + Na]^{+}$

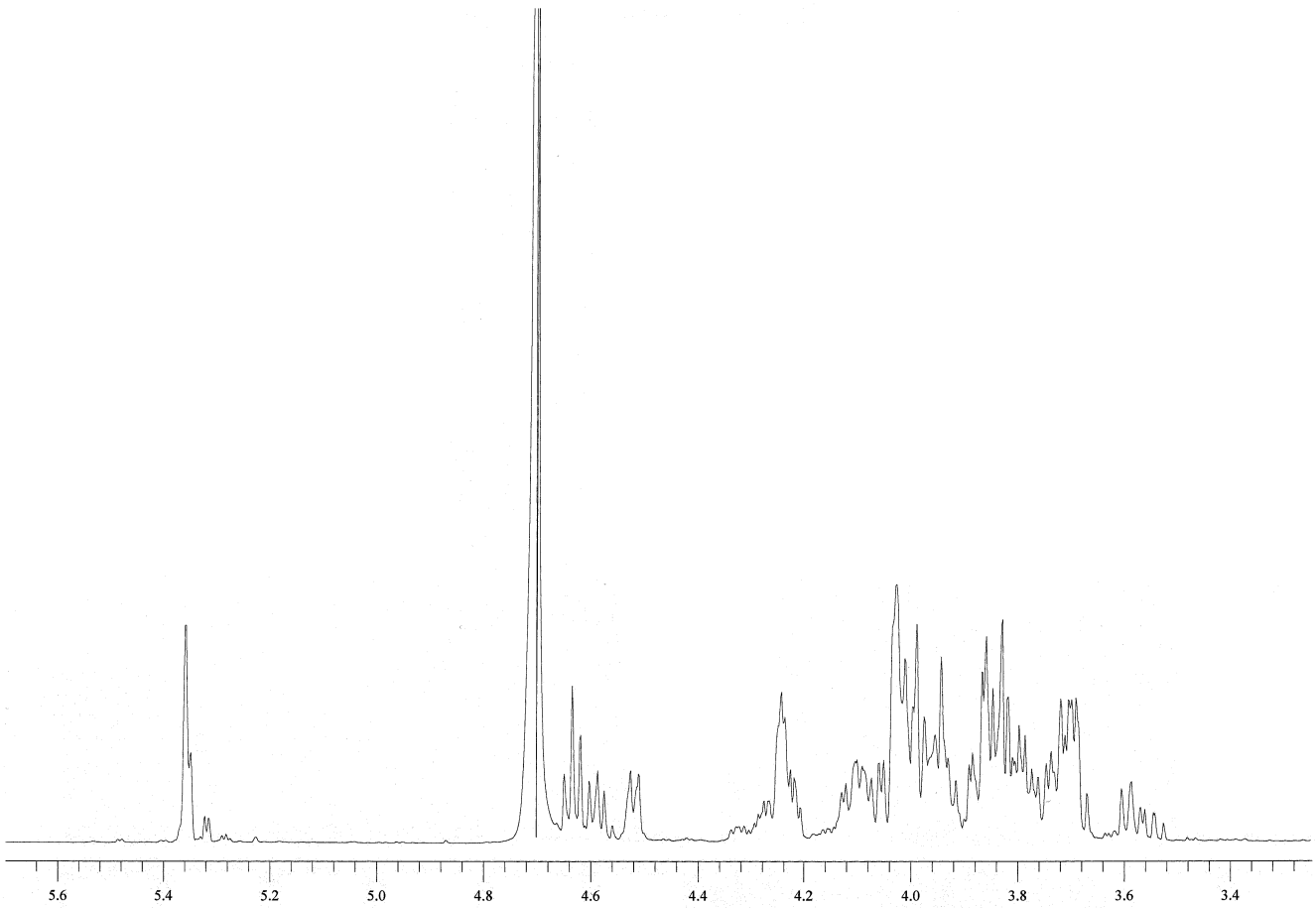


Fig. 2. 1D ^{1}H NMR spectrum of the free hexasaccharide **1**. The spectrum was acquired at 320 K and 500 MHz in D_2O.

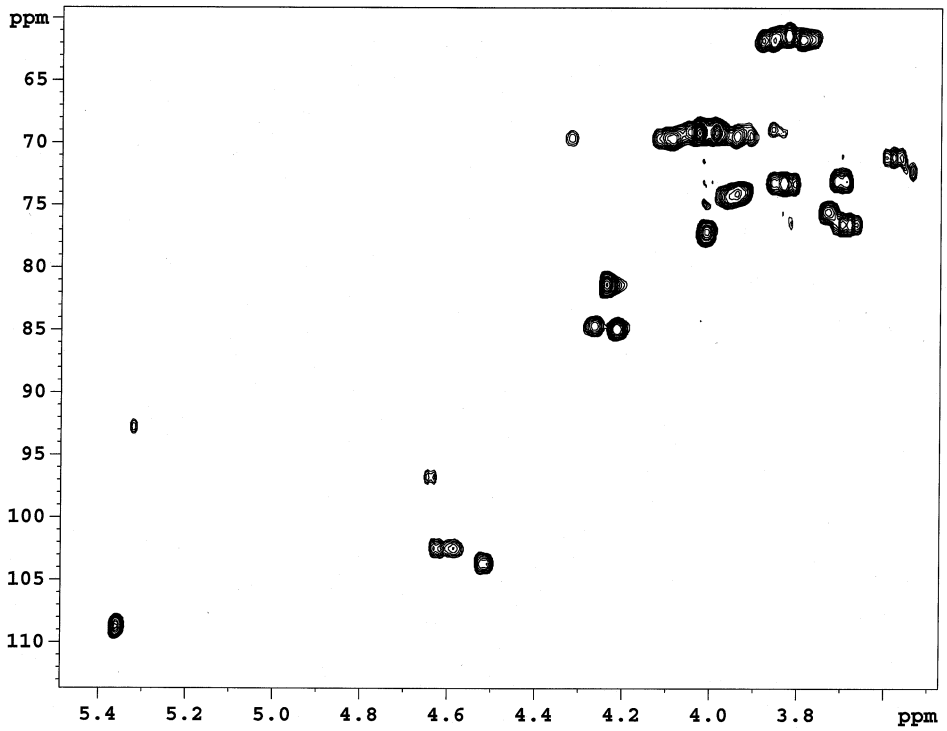


Fig. 3. 2D $^{1}H-^{13}C$ correlated NMR spectrum of the free hexasaccharide **1**. The spectrum was acquired at 298 K, 500/125 MHz in D_2O.

peaks using a 2,5-dihydroxybenzoic acid (DHB) matrix.

3,4,6-Tri-O-*acetyl-2*-O-*benzyl-β*-D-*galacto-pyranosyl-(1→6)-2,3,4-tri*-O-*acetyl-β*-D-*galactopyranosyl trichloroacetimidate* (**6**).—To a solution of **4**[8] (508 mg, 0.79 mmol) in dry *N*,*N*-DMF (1 mL) was added 97 mg of hydrazine acetate and the mixture was stirred for 1.5 h, until TLC showed a complete conversion (92:8, CH_2Cl_2–acetone, R_f 0.75). The mixture was diluted with 50 mL of CH_2Cl_2, washed twice with aq 10% NaCl and three times with water, dried over $MgSO_4$ and concentrated. The residue was purified by means of column chromatography (87:13, CH_2Cl_2–acetone) to yield **5** (235 mg, 50%). To a solution of **5** (235 mg, 0.33 mmol) in dry CH_2Cl_2 was added CCl_3CN (0.46 mL) and heated with K_2CO_3 (500 mg). Complete conversion was observed after 24 h (TLC: 92:8, CH_2Cl_2–acetone). The mixture was filtered through a pad of Celite, concentrated, and the product was purified by column chromatography (92:8, CH_2Cl_2–acetone) to yield **6** (197 mg, 70%); $[\alpha]_D$ +18.36° (*c* 0.41, $CHCl_3$); Anal. Calcd for $C_{33}H_{40}Cl_3NO_{17}$ (827.14): C, 47.87; H, 4.87. Found: C, 47.93; H, 4.88.

3,4,6-Tri-O-*acetyl-2*-O-*benzyl-β*-D-*galacto-pyranosyl-(1→6)-2,3,4-tri*-O-*acetyl-β*-D-*galactopyranosyl-(1→6)-2*-O-*benzyl-3,4*-O-*isopropylidene-β*-D-*galactopyranosyl-(1→6)-1,2:3,4-di*-O-*isopropylidene-α*-D-*galactopyranose* (**8**).—To a solution of **7**[8] (235 mg, 0.43 mmol) in dry CH_2Cl_2 (10 mL) were added compound **6** (0.43 g, 0.51 mmol, 1.2 equiv.) and 4 Å molecular sieves (600 mg), and the mixture was stirred for 1 h at rt. It was then cooled to −45 °C, and trimethylsilyl trifluormethanesulfonate (15 μL in 0.5 mL of dry CH_2Cl_2) was added. After 2 h 100 μL of triethylamine was added, the mixture was diluted with 40 mL of CH_2Cl_2, washed with water, dried, and concentrated. The crude product was purified by column chromatography (88:12, CH_2Cl_2–acetone) to give **8** (320 mg, 60%). $[\alpha]_D$ −1.63° (*c* 0.97, $CHCl_3$); Anal. Calcd for $C_{59}H_{78}O_{27}$ (1218.47): C, 58.11; H, 6.45. Found: C, 58.30; H, 6.44.

3,4,6-Tri-O-*acetyl-β*-D-*galactopyranosyl-(1→6)-2,3,4-tri*-O-*acetyl-β*-D-*galactopyranosyl-(1→6)-3,4*-O-*isopropylidene-β*-D-*galactopyranosyl-(1→6)-1,2:3,4-di*-O-*isopropylidene-α*-D-*galactopyranose* (**9**).—Palladium on activated charcoal (100 mg) was added to a solu-

tion of **8** (500 mg, 0.4 mmol) in EtOAc (5 mL). After hydrogenation for 12 h the mixture was diluted with EtOAc, filtered through a layer of Celite and concentrated. The product was purified by column chromatography (7:3, CH_2Cl_2–acetone) to obtain **9** (308 mg, 89%); $[\alpha]_D$ −22.37° (*c* 0.22, $CHCl_3$). Anal. Calcd for $C_{45}H_{66}O_{27}$ (1038.38): C, 51.98; H, 6.40. Found: C, 52.06; H, 6.39.

*2,3,5-Tri-*O*-benzoyl-α-*L*-arabinofuranosyl-(1→2)-3,4,6-tri-*O*-acetyl-β-*D*-galactopyranosyl-(1→6)-2,3,4-tri-*O*-acetyl-β-*D*-galactopyranosyl-(1→6)-[2,3,5-tri-*O*-benzoyl-α-*L*-arabinofuranosyl-(1→2)]-3,4-*O*-isopropylidene-β-*D*-galactopyranosyl-(1→6)-1,2:3,4-di-*O*-iso-*

Table 1
^{1}H NMR chemical shift- and $^3J_{H1,H2}$ coupling constant values for compounds **1** and **11**

Sugar ring	Carbon	δ (ppm)			$^3J_{H1,H2}$			
		11	**1**		**11**		**1**	
			α	β			α	β
	1	5.207	5.44	4.75	$J_{1,2}$	4.91	3.7	8.0
	2	4.113	3.99	3.68	$J_{2,3}$	7.88		
	3	4.477			$J_{3,4}$	2.36		
A	4	4.171			$J_{4,5}$	7.87		
	5	3.960			$J_{5,6}$	2.0		
	6	4.201			$J_{6,6'}$	10.4		
	6′	3.567						
	1	4.359	4.702		$J_{1,2}$	8.2	7.5	
	2	3.940	3.835		$J_{2,3}$	10.5		
	3	4.738	4.163		$J_{3,4}$	4.8		
B	4	4.078			$J_{4,5}$	10.3		
	5	3.931			$J_{5,6}$	6.1		
	6	4.048			$J_{6,6'}$	10.3		
	6′	3.780						
	1	5.679	5.48		$J_{1,2}$	>1	<3	
	2	5.066	4.37		$J_{2,3}$	3.5		
C	3	5.647	4.14		$J_{3,4}$	3.4		
	4	5.582	4.34		$J_{4,5}$	>1		
	5	4.895	3.9		$J_{5,5'}$	12.0		
	5′	4.825						
	1	4.647	4.63		$J_{1,2}$	8.0	7.5	
	2	5.093	3.73		$J_{2,3}$	9.5		
	3	5.210			$J_{3,4}$	3.6		
D	4	5.380			$J_{4,5}$	3.6		
	5	3.900			$J_{5,6}$	2.0		
	6	3.819			$J_{6,6'}$	10.4		
	6′	3.682						
	1	4.509	4.74		$J_{1,2}$	7.7	7.5	
	2	3.940	3.818		$J_{2,3}$	10.4		
	3	5.031	4.163		$J_{3,4}$	3.4		
E	4	5.474			$J_{4,5}$	3.6		
	5	3.989			$J_{5,6}$	1.8		
	6	4.130			$J_{6,6'}$	9.3		
	6′							
	1	5.495	5.48		$J_{1,2}$	>1	<3	
	2	5.066	4.37		$J_{2,3}$	3.4		
F	3	5.647	4.14		$J_{3,4}$	1.4		
	4	5.415	4.38		$J_{4,5}$	1.6		
	5	4.823	3.92		$J_{5,5'}$	12.1		
	5′	4.710						

Table 2
^{13}C NMR chemical shift- and $^{1}J_{C1,H1}$ coupling constant values for compounds **1**, **8**, **9**, and **11**

Sugar ring	Carbon	δ (ppm)					$^{1}J_{C1,H1}$ (Hz)	
		8	**9**	**11**	**1**		**1**	
					α	β	α	β
	1	96.27	96.15	96.77	93.05	97.09	170.2	161.4
	2	70.65	70.60	70.66	73.55	72.56		
	3	70.90	70.85	71.52				
A	4	70.35	70.29	72.27				
	5	67.52	67.35	67.96				
	6	68.91	68.90	70.36				
	1	103.27	103.05	102.01	102.72		161	
	2	78.01	71.04	75.40	73.32			
	3	78.66	78.81	81.65	69.51			
B	4	73.66	73.61	74.63				
	5	72.65	72.31	72.85				
	6	69.51	69.12	69.70				
	1			104.65	108.91		176	
	2			81.65	81.64			
C	3			78.41	77.54			
	4			83.14	85.21			
	5			64.20	61.89			
	1	101.27	101.22	102.01	103.88		161	
	2	71.88	71.85	71.60	71.44			
	3	68.75	68.69	69.63				
D	4	67.28	66.77	67.96				
	5	70.66	70.70	70.36				
	6	67.05	67.04	67.28				
	1	103.53	103.17	102.52	102.72		161	
	2	75.98	67.87	75.40	76.78			
	3	72.97	73.03	73.57	69.51			
E	4	68.91	68.90	68.32				
	5	73.66	73.15	73.15				
	6	61.22	61.31	62.02				
	1			106.72	108.91		176	
	2			81.15	81.64			
F	3			78.41	77.54			
	4			82.91	85.04			
	5			64.28	62.07			

*propylidene-α-*D*-galactopyranose* (**11**).—Powdered $Hg(CN)_2$ (162 mg, 0.64 mmol, 2.2 equiv.) and 4 Å molecular sieves were added to a solution of **9** (308 mg, 0.29 mmol) in dry CH_3CN (7 mL), the mixture was stirred for 3 h, and compound **10**[11] (0.748 g, 1.45 mmol, 5 equiv.) was added to the mixture. After 2 h TLC (9:1, CH_2Cl_2–acetone) showed a complete conversion. The mixture was diluted with CH_2Cl_2, the inorganic salts were filtered off, and the filtrate was concentrated. The residue was dissolved in 150 mL of CH_2Cl_2 and washed with aq 5% KI solution (4 × 25 mL) and water (2 × 25 mL). The organic layer was dried and concentrated. The syrupy residue was purified by column chromatography (93:7, CH_2Cl_2–acetone) to yield **11** (340 mg, 62.5%). $[\alpha]_D$ −7.36° (*c* 0.063, $CHCl_3$). MALDI-TOF MS: *m/z* 1949.33 $[M + Na]^+$, ($[C_{97}H_{106}O_{41} + Na]^+$ Calcd 1949.62), resolution 2700. ^1H and ^{13}C NMR data see in Table 1.

*α-*L*-Arabinofuranosyl-(1→2)-β-*D*-galacto-pyranosyl-(1→6)-β-*D*-galactopyranosyl-(1→6)*

-[α-L-arabinofuranosyl-(1→2)]-β-D-galacto-pyranosyl-(1→6)-α,β-D-galactose (**1**). —To a stirred solution of **11** (220 mg, 0.114 mmol) in 25 mL of CH_2Cl_2, 3.8 mL of trifluoroacetic acid and one drop of water were added. After 24 h triethylamine was added, the mixture was diluted with 75 mL of CH_2Cl_2, washed with aq $NaHCO_3$ solution (4×15 mL), and water (2×15 mL), dried and evaporated. To a stirred solution of the residue (180 mg) in dry MeOH (10 mL) was added NaOMe (pH ~ 8). After 12 h TLC (50:50:28, acetone–EtOH–water) showed a complete conversion. The solution was neutralized with Amberlite IR-120 H^+ ion-exchange resin, filtered and concentrated. The residue was dissolved in water (50 mL), washed with Et_2O (3×10 mL) and concentrated. The residue was purified by column chromatography (50:50:28, acetone–ethanol–water) to give **1** (94 mg, 88%); $[\alpha]_D$ $-31.43°$ (*c* 0.14, water). Characteristic ^{13}C NMR data: 92.8 (C-1α), 96.8 (C-1β), 102.5 (C-1′ and C-1‴), 103.7 (C-1″); 108.8 (C-1s of the Araf units). MALDI-TOF MS: *m/z* 953.34 $[M + Na]^+$, ($[C_{34}H_{58}O_{29} + Na]^+$ Calcd 953.30), resolution 3900.

Acknowledgements

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