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SYNTHESIS OF CYCLO-[(1-6)-β-D-GALACTOFURANO]-OLIGOSACCHARIDES

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Abstract - Synthesis is described of bifunctional di- and trisaccharide monomers built up of (1-6)-β-linked D-galactofuranose units and carrying 6-O-trityl and 1,2-O-(1-cyano)ethylidene groups at extreme termini. They are converted into cyclic oligosaccharides under the action of silver trifluoromethanesulfonate.

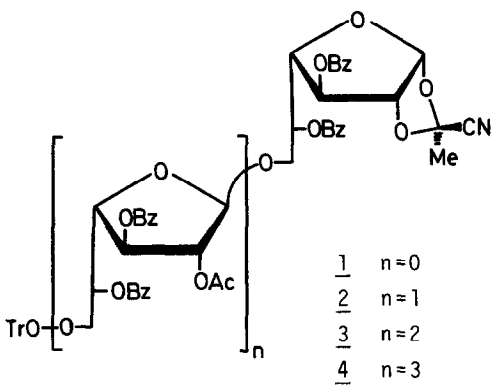
O-Tritylated 1,2-O-(1-cyano)ethylidene derivatives (CED) of mono- and oligosaccharides are known to serve as monomers in a triphenylmethylium perchlorate-catalysed polycondensation to give regular polysaccharides with 1,2-*trans*-glycosidic linkage between monomeric units[1]. This reaction results, as a rule, in formation of linear polysaccharides, the degree of polymerisation of which ranging from 10 to 50 per repeating unit. In majority of cases the linear character of polysaccharides is firmly established by methylation analysis and/or ^{13}C-NMR spectroscopy. At the same time the growing oligosaccharide chain can also undergo, in principle, intramolecular condensation which should yield cyclic oligosaccharides with various number of repeating units. The formation of products of this kind was observed by us[2] when polycondensation has been undertaken of 3- and 6-trityl ethers of 1,2-O-[1-(*exo*-cyano)-ethylidene]-α-D-galactofuranose. Thus, the monomer 1 gave, in the presence of silver trifluoromethanesulfonate (triflate) as an initiator, cyclo-oligogalactofuranoses 5-8 in yields of 5, 6, 10, and 1.7%, respectively, besides the linear (1-6)-β-D-galactofuranan. The structure of repeating units in this cyclic oligosaccharides was deduced from their ^{1}H- and ^{13}C-NMR spectra and the number of units followed from molecular mass determination by FAB-MS.

The natural cyclooligosaccharides (COS), cyclodextrins, together with their numerous synthetic derivatives are of great interest due to their ability to form inclusion complexes with various organic guest molecules[3]. Preparation of the synthetic COS can apparently broaden the existing family of molecules which manifest these properties.

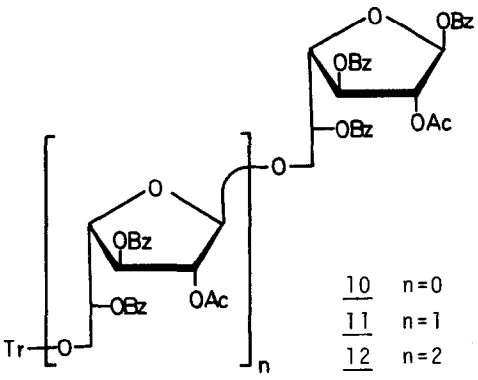
To achieve the yields of definite COS higher then those reported[2] it seemed preferable to start directly from the oligosaccharide monomers which contain the necessary number of the repeating units. Here we report the results of our studies aimed at preparing COS by cyclisation of tritylated CED of galactofuranooligosaccharides. Successful application of the direct cyclisation of bifunctional oligosaccharide derivatives was demonstrated by the synthesis of α- and γ-cyclodextrins from benzylated (α1-4)-D-gluco-hexa- and -octaosyl fluorides with a free hydroxyl group at C-4 of the terminal residue[4,5].

The oligomer-homologues of the monomer 1, viz., di-, tri-, and tetrasaccharide derivatives 2, 3, and 4, were prepared from 1 by interrupting its polycondensation after 4 hr

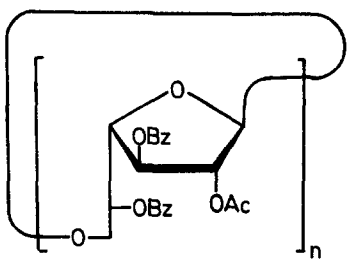
(normally it goes to completion in 40 hr). From a complex reaction mixture the target derivatives 2, 3, and 4 were isolated in the yields of 11, 8, and 3%, respectively, the recovery of the monomer 1 being 20%. Several minor side-products, viz., tritylated peracylated mono-, di-, and trisaccharides 10, 11, and 12 were also isolated together with the cyclic dimer 5 (5%).



1 n=0
2 n=1
3 n=2
4 n=3



10 n=0
11 n=1
12 n=2



5 n=2
6 n=3
7 n=4
8 n=5
9 n=6

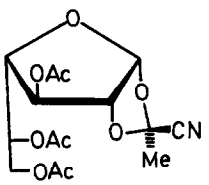
The structure of the monomers 2-4 was confirmed by NMR spectral data. Signals for H-1 - - H-4 were characteristic in the ^{1}H-NMR spectra. For the "reducing" terminus the signals for H-1 and H-2 were doublets, H-3 was a singlet, and H-4 was a broadened doublet. For the inner and terminal nonreducing residues H-1 and H-2 were singlets, H-3 was a doublet, and H-4 was a pseudotriplet. The number of units in these oligosaccharide derivatives was easily countable from the number of sets of signals for H-1 - H-6 (those for H-5 at δ 5.8-6.0 being the most characteristic) and for the methyl groups which resonated at δ 1.6-1.7 (CH_3CO) and 1.98 (cyanoethylidene group). Their ^{13}C-NMR spectra exhibited characteristic signals for the CH_3-C-CN moiety (δ 24.2, 101.2, and 116.6) and O-trityl group (δ 143.7 for C-1 of phenyls and ca. 87 for Ph_3CO, this signal overlapped in some cases with those for C-4).

Spectral data for 10-12 pointed to the presence of the 1-O-benzoyl and 2-O-acetyl groups at the "reducing" end. This followed from a down-field position for H-1 (δ 6.6) and the integral intensities for the aromatic and acetyl protons. That these groups were trans (β-configuration) evidenced from both the chemical shift for C-1 (δ 99 , cf. ref.6) and

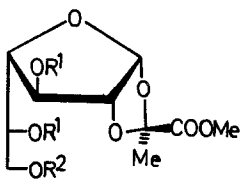
the fact that the signal for H-1 was a singlet. The formation of 1-O-acyl derivatives as side-products in glycosylations with CED is documented[7]. This can be one of the reasons for the block of a growth of a polysaccharide chain upon polycondensation of the tritylated CED as monomers.

Since the above approach to obtain the oligosaccharide monomers proved to be rather inefficient, an alternative route to their preparation was developed. This consisted in a stepwise elongation of an oligosaccharide chain starting from derivatives bearing 1,2-O-(1-methoxycarbonyl)ethylidene group as a temporary substitute for the 1,2-O-(1-cyano)ethylidene function taking into account the possibility for smooth two-step one-pot conversion of the former into the latter. This involves ammonolysis and treatment with benzoyl chloride in pyridine which results in both dehydration of the amide into nitrile function and O-benzoylation[8,9].

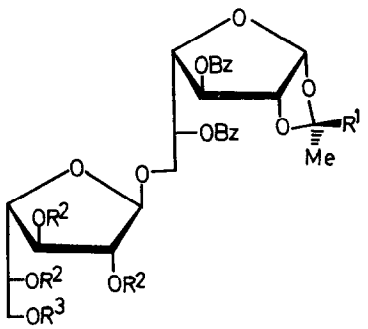
Treatment of the known 13 with methanolic 0.05 M MeONa gave[9] 1,2-O-(1-methoxycarbonyl)-ethylidene-α-D-galactofuranose 14 which was converted into 6-trityl ether 15 and then into dibenzoate 16. It was glycosylated with 13 in dichloromethane in the presence of silver triflate (0.1 equiv.) using vacuum technique[10] to give the disaccharide derivative 17 in 80% yield. This was subjected to Zemplen deacylation and selective tritylation followed by treatment with benzoyl chloride in pyridine either directly (to give the 6-trityl ether 18) or after prior ammonolysis to give the monomer 19.



13



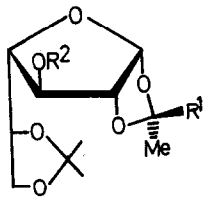
14 $R^1=R^2=H$
15 $R^1=H$, $R^2=Tr$
16 $R^1=Bz$, $R^2=Tr$



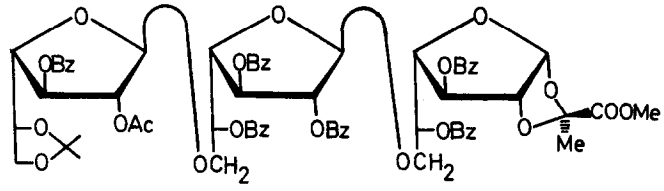
17 $R^1=COOMe$, $R^2=R^3=Ac$
18 $R^1=COOMe$, $R^2=Bz$, $R^3=Tr$
19 $R^1=CN$, $R^2=Bz$, $R^3=Tr$

The known[9] 1,2-O-(1-methoxycarbonyl)ethylidene derivative 20 was conventionally converted into CED 21. Its reaction with the trityl ether 18 afforded the trisaccharide derivative 22 in a good yield. Compound 21 and not 13 was chosen as a glycosyl-donor in view of possibility of easier liberation of 6"-OH without affecting other (but 5"-) O-protecting groups. The trisaccharide monomer 23 was obtained from its precursor 22 in four steps by successive, one-pot deacetonation with methanolic toluene-p-sulfonic acid, selective tritylati-

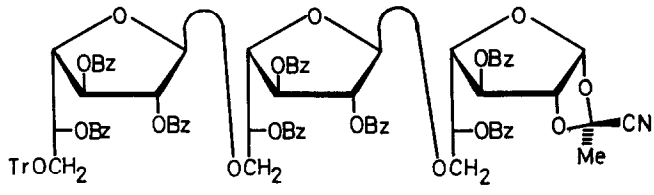
on, ammonolysis, and treatment with benzoyl chloride in pyridine, the overall yield being 67%. The NMR spectra of the monomers 19 and 23 were similar to those of 2 and 3 that proves their structure. Spectral regularities found for the oligosaccharide CED hold for the (1-methoxycarbonyl)ethylidene derivatives 16-18, 20, and 22 as regards chemical shifts and coupling constants, the methoxycarbonylethylidene group itself being characterised by δ(H) 3.75 (CH_3O) and δ(C) 21.4, 108-108.5, and 52.5-52.6 ($\underline{CH_3}$-$\underline{C}$-COO$\underline{CH_3}$).



20 R^1=COOMe, R^2=H
21 R^1=CN, R^2=Bz



22



23

Condensation of each of the monomers 2, 3, and 4 in dichloromethane in the presence of silver triflate resulted in formation of several products. TLC analysis with COS obtained upon polycondensation of the monomer 1 (ref. 2) as standards revealed that the disaccharide monomer 2 was converted into a mixture of dimer 5, tetramer 7, and hexamer 9. The trisaccharide monomer 3 gave trimer 6 and hexamer 9, while tetramer 7 was detected as a product of condensation of the tetrasaccharide monomer 4. In each case were present products with lower chromatographic mobility.

The previously isolated[2] protected COS 5-8 were deacylated and the free COS 24-27 obtained were characterised by ^{13}C-NMR spectra (Table 1) and elution volumes upon gel-permeation chromatography (Table 2). As can be seen, the COS were eluted later than the linear oligosaccharides of the [-6)Glc(α1-4)Glc(β1-]$_n$ series[11] with similar molecular mass. The reaction mixtures obtained upon condensation of the monomers 2, 3, and 4 were separately deacylated and analysed by gel-permeation chromatography. The last-eluted peaks coincided in elution volumes with those for authentic COS 24, 25, and 26, respectively, that proves additionally the size of macrocycles in compounds 5-7.

The preparative-scale synthesis of COS was performed starting from the monomers 19 and 23. To increase the yield of cyclic products and decelerate "linear" polycondensation the reactions were run under conditions which differed from those employed earlier[9], viz., the concentration of the monomers was ca. 10-fold less with the monomer:initiator ratio of 1:1

(to achieve reasonable reaction rate) instead of 10:1.

Table 1. ^{13}C-NMR data of compounds 24 - 30 (δ in p.p.m.)*

Compound	C-1	C-2	C-3	C-4	C-5	C-6
24	107.5	80.0	77.2	84.6	66.95	66.5
25	108.3	82.65	77.0	82.5	68.9	69.7
26	108.8	82.35	77.8	83.65	69.0	69.5
27	109.0	82.2	77.9	84.25	70.1	70.0
28	109.0	82.2	78.0	84.3	70.25	70.65
29	109.1	82.4	78.1	84.4	70.4	70.7
30	109.1	82.2	77.9	84.2	70.2	70.2
(1-6)-β-D-galactofuranan	109.1	82.3	78.2	84.4	70.9	70.4

* Assignment of signals for C-5 and C-6 (except for 25) may be interchanged.

Table 2. Elution volumes (at peak maxima) for COS 24 - 30 and oligosaccharides of [-6)Mal(β1-]$_n$-series[11]

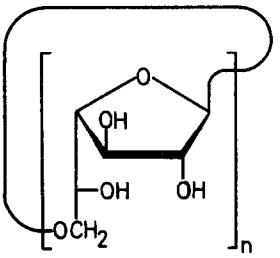
Compound	24	25	26	27	28	29	30	[-6)Mal(β1-]$_n$			
n	2	3	4	5	6	8	9	1	2	3	4
Mol.mass	324	486	648	810	972	1296	1458	342	666	990	1314
Elution volume (ml)	124	111	103	97	91	86	84	107	94	88.5	80.5

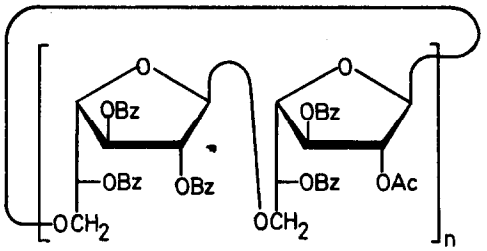
Interaction of the disaccharide monomer 19 with silver triflate under these conditions yielded, besides a high-molecular-weight fraction which was not investigated further, four products isolated by column chromatography. Judging from their TLC-mobilities and ^{1}H-NMR spectra they were COS 31-34. Each of them exhibited in the ^{1}H-NMR spectrum two sets of signals for H-1 - H-6 of the galactofuranose residue. Assignment of signals to 2-O-acetyl and 2-O-benzoyl moieties was made with the use of spectral data for 5 - 7 (ref. 2).

Zemplen deacylation of 31-34 gave the free COS 24, 26, 28, and 29, respectively. Coincidence of the elution volumes for the samples of 24 and 26 prepared from either 1 or 19 proves their structures as a dimer and tetramer. Additionally, the size of macrocycles in 24-27 was determined by electron-impact mass-spectrometry of permethylated derivatives prepared by Hakomori methylation procedure[12]. Mass-spectra of per-O-methyl-24, -25, and -26 contained $[M]^+$-ions at m/z 408, 612, and 816, respectively. The peak of $[M]^+$-ion was absent from the spectrum of per-O-methyl-27 and the highest-mass peak at m/z 988 corresponded to $[M\text{-MeOH}]^+$-ion. Analogous peaks were also detected in the spectra of permethylated 24-26.

Cyclisation of the monomer 23 was carried out under similar conditions. A set of products was obtained, which differed in TLC-mobility, along with a high-molecular-weight pro-

duct. This mixture following deacylation was subjected to gel-permeation chromatography to give COS 25, 28, and 30 in 24, 23.6, and 17% yield. Their structures were ascertained from elution volumes, compounds 25 and 28 prepared from 23 being eluted with the same volumes as the trimer from 1 and hexamer from 19, respectively.





24	n=2	31	n=1
25	n=3	32	n=2
26	n=4	33	n=3
27	n=5	34	n=4
28	n=6		
29	n=8		
30	n=9		

Listed in Table 1 are the ^{13}C-NMR data for all the COS synthesised. As can be seen, differences in chemical shifts for COS comprising more than three sugar units are rather small and the very chemical shifts are close to those for the linear (1-6)-β-D-galactofuranan (DP ca. 30)[9]. This reflects structural similarity of the COS obtained.

The results of this study demonstrate that the intramolecular cyclisation of tritylated cyanoethylidene derivatives of oligosaccharides can compete with the "linear" polycondensation. This allows to use the above derivatives in the synthesis of 1,2-*trans*-linked cyclic oligosaccharides. The monomers 19 and 23 do not produce cyclic dimer and trimer solely, possibly due to intrinsic strain, which results thereby in formation of cyclic oligomer-homologues and high-molecular-weight products.

EXPERIMENTAL

Optical rotations were measured with a JASCO DIP-360 automatic digital polarimeter for soln in chloroform (in water for free COS) at 25±2°C. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a Bruker WM-250 or AM-300 instrument in $CDCl_3$ (internal TMS) or in D_2O (internal MeOH, δ_{TMS} 50.15). Coupling constants (in Hz) are first order. Mass-spectra were recorded with a Varian MAT 311 spectrometer. Column chromatography was performed on silica gel L 40/100 um (CSSR) using gradient elution from benzene to benzene-ethyl acetate 4:1. All glycosylations were carried out using vacuum technique[10]. TLC was performed on Kieselgel 60 (Merck) plates using solvent systems A, toluene-ethyl acetate 9:1; B, benzene-ethyl ace-

tate 85:15; C, heptane-ethyl acetate 3:2; D, n-butanol-ethanol-water 3:3:2, followed by charring with sulfuric acid. HPLC was performed on a Silasorb 60 column using heptane-ethyl acetate as an eluent. Gel-permeation chromatography was performed on a column (1.6 x 76 cm) with Fractogel TSK HW-40(S) in 0.1 M acetic acid, differential refractometer Knauer 88.00 was used to monitor separations. Concentrations were performed in vacuo at 40°C. All compounds synthesised were amorphous powders.

Synthesis of the monomers 2, 3, and 4 by polycondensation of 3,5-di-O-benzoyl-1,2-O-[1-(exo-cyano)ethylidene]-6-O-trityl-α-D-galactofuranose 1. Polycondensation of the monomer 1 (3.44 g, 5.0 mmol) in dichloromethane (20 ml) in the presence of silver triflate (129 mg, 0.5mmol) was carried out at 20°C and quenched after 4 hr by addition of pyridine (0.5 ml). The reaction mixture was diluted with chloroform (180 ml), washed with 10% aq $Na_2S_2O_3$ (2 x 50 ml) and water, dried, and concentrated. Column chromatography afforded a mixture of compounds with R_1 values of 0.3 - 1 (B). Separation by HPLC gave 1 (680 mg, 20%), 2 - 4 and 10 - 12.

2, yield 290 mg (10.6%), R_f 0.59 (B), $[\alpha]_D$ -16° (c 1.13). ^{1}H-NMR: δ 6.14 (d, 1H, $J_{1,2}$ 4.4, H-1), 5.93 (ddd, 1H, $J_{5,4}$ 4.1, $J_{5,6a}$ 6.5, $J_{5,6b}$ 4.4, H-5'), 5.70 (d, 1H, $J_{3,4}$ 1.0, H-3), 5.52 (ddd, 1H, $J_{5,4}$ 9.4, $J_{5,6a}$ 6.5, $J_{5,6b}$ 4.0, H-5), 5.25 (s, 1H, H-1'), 5.24 (d, 1H, $J_{3,4}$ 4.1, H-3'), 5.20 (s, 1H, H-2'), 4.87 (d, 1H, H-2), 4.83 (t, 1H, H-4'), 4.66 (bd, 1H, H-4), 4.12 (m, 1H, H-6a), 3.74 (dd, 1H, $J_{6a,6b}$ 10.7, H-6b), 3.55 (dd, 1H, $J_{6a,6b}$ 10.2, H-6a'), 3.42 (dd, 1H, H-6b'), 1.98 (s, 3H, CH_3CCN), 1.72 (s, 3H, CH_3CO). ^{13}C-NMR: δ 169.4 ($CH_3\underline{C}O$), 165.9 (Ph$\underline{C}$O), 143.7 (Tr), 107.5 (C-1), 105.9 (C-1'), 87.0 (C-4), 86.8 (Ph$_3\underline{C}$O), 85.45 (C-2), 82.6 (C-4'), 80.8 (C-2'), 78.3 (C-3'), 76.0 (C-3), 72.3 (C-5'), 71.2 (C-5), 66.0 (C-6), 63.0 (C-6'), 24.2, 101.1, 116.6 (CH_3-$\underline{C}$-CN), 20.2 ($\underline{C}H_3CO$).

3, yield 210 mg (8.4%), R_f 0.42 (B), $[\alpha]_D$ -35° (c 0.87). ^{1}H-NMR: δ 6.14 (d, 1H, $J_{1,2}$ 4.1, H-1), 5.93 (m, 1H, H-5"), 5.81 (m, 1H, H-5'), 5.68 (d, 1H, $J_{3,4}$ 1.0, H-3), 5.50 (m, 1H, H-5), 5.32 (bd, 1H, $J_{3,4}$ 3.9, H-3"), 5.28 (bd, 1H, $J_{3,4}$ 5.0, H-3'), 5.28 (bs, 1H, H-2"), 5.23 (s, 1H, H-1'), 5.15 (s, 1H, H-1"), 5.11 (d, 1H, $J_{2,3}$ 1.2, H-2'), 4.85 (d, 1H, H-2), 4.75 (dd, 1H, $J_{4,5}$ 3.0, H-4"), 4.68 (dd, 1H, $J_{4,5}$ 3.9, H-4'), 4.65 (bd, 1H, $J_{4,5}$ 8.5, H-4), 4.15, 4.03, 3.93 (3dd, 3 x 1H, H-6a,6a',6b'), 3.74 (dd, 1H, $J_{5,6b}$ 3.5, $J_{6a,6b}$ 10.8, H-6b), 3.54 (dd, 1H, $J_{5,6a}$ 6.0, H-6a"), 3.42 (dd, 1H, $J_{5,6b}$ 4.2, H-6b"), 1.98 (s, 3H, CH_3CCN), 1.67, 1.65 (2s, 2 x 3H, CH_3CO). ^{13}C-NMR: δ 169.2 ($CH_3\underline{C}O$), 165.7 - 165.4 (Ph$\underline{C}$O), 143.7 (Tr), 106.5 (C-1), 106.3 x 2 (C-1',1"), 88.9 (C-4), 88.8 (Ph$_3\underline{C}$O), 85.6 (C-2), 82.7 (C-2"), 82.0 (C-2'), 81.3 (C-4'), 80.8 (C-4"), 78.1 (C-3"), 77.8 (C-3'), 76.2 (C-3), 72.2 (C-5"), 71.4, 71.3 (C-5,5'), 66.4 x 2 (C-6,6'), 62.9 (C-6"), 24.3,101.2,116.6 (CH_3-$\underline{C}$-CN), 20.2 ($\underline{C}H_3CO$).

4, yield 80 mg (3.3%), R_f 0.27 (B), $[\alpha]_D$ -52.5° (c1.14). ^{1}H-NMR: δ 6.14 (d, 1H, $J_{1,2}$ 4.2, H-1), 5.96, 5.86, 5.78 (3m, 3 x 1H, H-5',5",5'"), 5.69 (bs, 1H, H-3'"), 5.50 (m, 1H, H-5), 5.36 (bd, 1H, $J_{3,4}$ 4.5, H-3), 5.28 (s, 1H, H-2'"), 5.26 (m, 2H, H-3',3"), 5.25 (s,1H, H-1'), 5.19 (s, 1H, H-2"), 5.11 (s, 2H, H-1",1'"), 5.09 (d, 1H, $J_{2,3}$ 1.2, H-2'), 4.85 (d, 1H, H-2), 4.73 - 4.61 (m, 4H, H-4,4',4",4'"), 4-22 - 3.90 (m, 5H, H-6a,6a',6b',6a",6b"), 3.78 (dd, 1H, $J_{5,6b}$ 3.7, $J_{6a,6b}$ 10.7, H-6b), 3.53 (dd, 1H, $J_{5,6a}$ 6.5, $J_{6a,6b}$ 9.8, H-6a'"), 3.40 (dd, 1H, $J_{5,6b}$ 4.1, H-6b'"), 1.98 (s, 3H, CH_3CCN), 1.68, 1.66, 1.63 (3s, 9H, CH_3CO).

10, yield 140 mg (3%), R_f 0.71 (B), $[\alpha]_D$ -38.5° (c 1.06). ^{1}H-NMR: δ 6.69 (s, 1H, H-1), 6.03 (m, 1H, H-5), 5.58 (d, 1H, $J_{3,4}$ 3.5, H-3), 5.57 (s, 1H, H-2), 4.97 (t, 1H, H-4), 3.70 (dd, 1H, $J_{5,6a}$ 7.0, $J_{6a,6b}$ 10.0, H-6a), 3.56 (dd, 1H, $J_{5,6b}$ 4.8, H-6b), 1.80 (s, 3H, CH_3CO). ^{13}C-NMR: δ 169.3 ($CH_3\underline{C}O$), 165.7 (Ph$\underline{C}$O), 143.55 (Tr), 99.65 (C-1), 84.7 (C-4), 80.1 (C-2), 77.8 (C-3), 71.9 (C-5), 62.9 (C-6), 20.2 ($\underline{C}H_3CO$).

11, yield 40 mg (1.3%), R_f 0.48 (B), $[\alpha]_D$ -57° (c 1.08). ^{1}H-NMR: δ 6.57 (s, 1H, H-1), 5.90 - 5.77 (2m, 2H, H-5,5'), 5.47 (m, 2H, H-2,3), 5.26 (bd, 1H, $J_{3,4}$ 4.5, H-3'), 5.15 (s, 1H, H-1'), 5.11 (d, 1H, $J_{2,3}$ 1.2, H-2'), 4.76 (t, 1H, $J_{4,3}=J_{4,5}$=3.3, H-4), 4.66 (dd, 1H, $J_{4,5}$ 3.5, H-4'), 4.08 (m, 1H, H-6a), 3.93 (dd, 1H, $J_{5,6b}$ 6.8, $J_{6a,6b}$ 10.5, H-6b), 3.52 (dd, 1H, $J_{5,6a}$ 4.0, $J_{6a,6b}$ 9.1, H-6a'), 3.39 (dd, 1H, $J_{5,6b}$ 4.4, H-6b'), 1.78, 1.69 (2s, 2 x 3H, CH_3CO). ^{13}C-NMR: δ 165.8 (Ph$\underline{C}$O), 143.75 (Tr), 106.0 (C-1'), 99.95 (C-1), 84.8 (C-4'), 82.1 (C-4), 81.3(C-2'), 80.2, 77.8 (C-2,3), 77.1 (C-3'), 72.1 (C-5'), 71.1 (C-5), 65.7 (C-6), 62.8 (C-6'), 20.2 ($\underline{C}H_3CO$).

12, yield 40 mg (1.5%), R_f 0.33 (B), $[\alpha]_D$ -61° (c 1.55). ^{1}H-NMR: δ 6.56 (s, 1H, H-1), 5.95 - 5.77 (m, 3H, H-5,5',5"), 5.51 (bd, 1H, $J_{3,4}$ 3.2, H-3), 5.50 (s, 1H, H-2), 5.33 (bd, 1H, $J_{3,4}$ 4.2, H-3'), 5.28 (bd, 1H, $J_{3,4}$ 4.6, H-3"), 5.20, 5.16 (2s, 2 x 1H, H-1',1"), 5.13 (d, 1H, $J_{2,3}$ 1.0, H-2'), 5.11 (d, 1H, $J_{2,3}$1.0, H-2"), 4.76 (t, 1H, H-4), 4.69 (t, 1H, H-4"), 4.57 (dd, 1H, $J_{4,5}$ 3.2, H-4'), 4.09 (m, 2H, H-6a,6a'), 3.94 (dd, 2H, $J_{5,6b}$ 7.5, $J_{6a,6b}$ 10.8, H-6b,6b'), 3.54 (dd, 1H, $J_{5,6a}$ 6.8, $J_{6a,6b}$ 10.0, H-6a"), 3.42 (dd, 1H, $J_{5,6b}$ 4.5, H-6b"), 1.78, 1.67 x 2 (2s, 9H, CH_3CO).

Cyclo-[(1-6)-2-O-acetyl-3,5-di-O-benzoyl-β-D-galactofurano]-pentaose 8 was isolated by HPLC from a mixture of products of polycondensation [2,9] of the monomer 1, yield 1.7%, $[\alpha]_D$ -81° (c 1.07). ^{1}H-NMR: δ 5.85 (m, 1H, H-5), 5.28 (dd, 1H, $J_{2,3}$ 1.1, $J_{3,4}$ 4.5, H-3), 5.23 (s, 1H, H-1), 5.15 (d, 1H, H-2), 4.59 (dd, 1H, $J_{4,5}$ 2.2, H-4), 4.09 (dd, 1H, $J_{5,6a}$ 8.1, $J_{6a,6b}$ 11.4, H-6a), 3.96 (dd, 1H, $J_{5,6b}$ 4.9, H-6b), 1.64 (s, 3H, CH_3CO). Deacylation of 8 with methanolic 0.1 M MeONa (4 hr) afforded the pentamer 27, $[\alpha]_D$ -6.6° [8] (c 0.84).

3,5-Di-O-benzoyl-1,2-O-[1-(exo-methoxycarbonyl)ethylidene]-6-O-trityl-α-D-galactofuranose 16. A soln of CED 13 (3.57 g, 10 mmol) in methanolic 0.05 M MeONa (50 ml) was kept at RT for 2 hr, neutralised with a cation-exchange resin KU-2(H^+), the resin was filtered off, washed with methanol and the combined filtrate and washings were concentrated. The residue was dried *in vacuo* and dissolved in pyridine (8 ml). Triphenylchloromethane (3.34 g, 12 mmol) was added, the soln was kept at RT for 17 hr, diluted with chloroform (100 ml), washed with water (3 x 30 ml), and concentrated. Column chromatography then gave the trityl ether 15, R_f 0.19 (A), $[\alpha]_D$ -5° (c 1.0). This was benzoylated with benzoyl chloride (1.6 ml) in pyridine (20 ml) to give following conventional work-up and HPLC the title derivative 16, yield 3.95 g (58%), R_f 0.62 (A). ^{1}H-NMR: δ 6.22 (d, 1H, $J_{1,2}$ 4.0, H-1), 5.61 (m, 1H, H-5), 5.42 (d, 1H, $J_{3,4}$ 1.3, H-3), 5.11 (bd, 1H, $J_{4,5}$ 10.0, H-4), 4.91 (d, 1H, H-2), 4.61 (dd, 1H, $J_{5,6a}$ 4.2, $J_{6a,6b}$ 11.5, H-6a), 4.35 (dd, 1H, $J_{5,6b}$ 2.9, H-6b), 3.74 (s, 3H, OCH_3), 1.81 (s, 3H, CH_3C). ^{13}C-NMR: δ 165.8, 165.0 (Ph$\underline{C}$O), 143.45 (Tr), 107.0 (C-1), 86.9 ($Ph_3\underline{C}O$), 86.1 (C-2), 85.6 (C-4), 76.8 (C-3), 73.0 (C-5), 63.6 (C-6), 21.4, 108.3, 169.1, 54.45 (CH_3-C-$COOCH_3$).

3,5-Di-O-benzoyl-1,2-O-[1-(exo-methoxycarbonyl)ethylidene]-6-O-(2,3,5,6-tetra-O-acetyl-β-D-galactofuranosyl)-α-D-galactofuranose 17. Glycosylation of the trityl ether 16 (3.65 g, 5.35 mmol) with CED 13 (1.69 g, 4.73 mmol) was carried out in the presence of silver triflate (129 mg, 0.5 mmol) in dichloromethane (16.5 ml). After 40 hr pyridine (0.3 ml) was added to the broght-yellow soln, the discoloured reaction mixture was diluted with chloroform (200 ml), washed with 10% aq $Na_2S_2O_3$ (70 ml) and water (2 x 70 ml), concentrated, and the residue was chromatographed to give 3.20 g (84%) of the disaccharide derivative 17, R_f 0.20 (A), $[\alpha]_D$ -30° (c 1.02). ^{1}H-NMR: δ 6.22 (d, 1H, $J_{1,2}$ 3.9, H-1), 5.62 (d, 1H, $J_{3,2}$ 1.5, H-3), 5.60 (m. 1H, H-5), 5.35 (m, 1H, H-5'), 5.14 (s, 1H, H-1'), 5.07 (d, 1H, $J_{2,3}$ 1.8, H-2'), 5.02 (d, 1H, H-2), 4.95 (dd, 1H, $J_{3,4}$ 5.4, H-3'), 4.66 (bd, 1H, $J_{4,5}$ 9.0, H-4), 4.33 (dd,1H, $J_{4,5}$ 3.6, H-4'), 4.29 (dd, 1H, $J_{5,6a}$ 4.3, $J_{6a,6b}$ 11.9, H-6a'), 4.15 (dd, 1H, $J_{5,6b}$ 7.4, H-6b'), 4.14 (dd, 1H, $J_{5,6a}$ 5.0, $J_{6a,6b}$ 11.0, H-6a), 3.84 (dd. 1H, $J_{5,6b}$ 4.4, H-6b), 3.76 (s, 3H, OCH_3), 2.11, 2.04, 2.01, 1.98 (4s, 4 x 3H, CH_3CO), 1.83 (s, 3H, CH_3C).

3,5-Di-O-benzoyl-1,2-O-[1-(exo-methoxycarbonyl)ethylidene]-6-O-(2,3,5-tri-O-benzoyl-6-O-trityl-β-D-galactofuranosyl)-α-D-galactofuranose 18. The above derivative 17 (2.89 g, 3.60 mmol) was deacylated with methanolic 0.05 M MeONa (60 ml) for 45 min, neutralised with KU-2 (H^+) resin as above, and the residue was treated with triphenylchloromethane (1.11 g, 4.0 mmol) in pyridine (9 ml) overnight. Following conventional work-up and benzoylation 18 was isolated by column chromatography, yield 2.72 g (64%), R_f 0.76 (A), $[\alpha]_D$ -16° (c 1.04). ^{1}H-NMR: δ 6.23 (d, 1H, $J_{1,2}$ 4.0, H-1), 5.92 (m, 1H, H-5'), 5.69 (d, 1H, $J_{3,4}$ 1.3, H-3), 5.67 (m, 1H, H-5), 5.57 (s, 1H, H-1'), 5.45 (d. 1H, $J_{3,4}$ 4.5, H-3'), 5.39 (s, 1H, H-2'), 4.99 (d, 1H, H-2), 4.86 (t, 1H, H-4'), 4.74 (bd, 1H, $J_{4,5}$ 9.0, H-4), 4.22 (dd, 1H, $J_{5,6a}$ 5.5, $J_{6a,6b}$ 11.0, H-6a), 3.89 (dd, 1H, $J_{5,6b}$ 3.7, H-6b), 3.67 (s, 3H, OCH_3), 3.58 (dd, 1H, $J_{5,6a}$ 6.8, $J_{6a,6b}$ 10.0, H-6a'), 3.45 (dd, 1H, $J_{5,6b}$ 4.3, H-6b'), 1.88 (s, 3H, CH_3C). ^{13}C-NMR: δ 165.8, 165.2 (PhCO), 143.6 (Tr), 107.2 (C-1), 105.9 (C-1'), 86.8 (Ph_3CO), 86.2 x 2 (C-2,4), 82.0x2 (C-2',4'), 78.0 (C-3'), 76.6 (C-3), 72.7, 72.3 (C-5,5'), 65.95 (C-6), 63.0 (C-6'), 21.35, 108.5, 169.2, 52.6 (CH_3-C-$COOCH_3$).

Conversion of 1,2-O-(1-methoxycarbonyl)ethylidene derivatives into 1,2-O-(1-cyano)ethylidene derivatives. General procedure (ref. 8,9). Methanolic soln of a methoxycarbonylethylidene derivative (1 mmol/5 ml) was saturated with ammonia at -5 - -10°C and left overnight at RT. Following concentration the residue was dissolved in pyridine (2 - 4 ml) and treated with benzoyl chloride (0.6 - 1.6 ml). After 17 hr at RT the excess of the reagent was decomposed by addition, at 0°C, of water (0.5 - 1.0 ml), the mixture was diluted with chloroform (50 ml) and washed with satd aq $NaHCO_3$ and water. The soln was concentrated and chromatographed.

3,5-Di-O-benzoyl-1,2-O-[1-(exo-cyano)ethylidene]-6-O-(2,3,5-tri-O-benzoyl-6-O-trityl-β-D-galactofuranosyl)-α-D-galactofuranose 19. Compound 17 was deacylated and tritylated as described in the synthesis of 18 and the product obtained was converted into CED 19 following the procedure indicated above. The yield of 19 was 75%, R_f 0.63 (A), $[\alpha]_D$ -12° (c 1.5). ^{1}H-NMR: δ 6.16 (d, 1H, $J_{1,2}$ 4.0, H-1), 5.92 (m, 1H, H-5'), 5.72 (s, 1H, H-3), 5.54 (m, 1H,H-5), 5.45 (bs, 1H, H-2'), 5.42 (bd, 1H, $J_{3,4}$ 4.7, H-3'), 5.35 (s, 1H, H-1'), 4.92 (d, 1H, H-2),

4.87 (t, 1H, H-4'), 4.71 (d, 1H, $J_{4,5}$ 9.0, H-4), 4.14 (dd, 1H, $J_{5,6a}$ 5.5, $J_{6a,6b}$ 10.9, H-6a), 3.80 (dd, 1H, $J_{5,6b}$ 4.0, H-6b), 3.56 (dd, 1H, $J_{5,6a}$ 6.8, $J_{6a,6b}$ 9.9, H-6a'), 3.45 (dd, 1H, $J_{5,6b}$ 4.4, H-6b'), 1.97 (s, 3H, CH_3CCN). ^{13}C-NMR: δ 156.6 (PhCO), 143.7 (Tr), 106.6 (C-1'), 106.0 (C-1), 86.9 (C-4), 85.55 (C-2), 82.2, 81.9 (C-2',4'), 78.1 (C-3'), 76.1 (C-3), 72.4 (C-5), 71.2 (C-5'), 66.05 (C-6), 63.05 (C-6'), 24.2, 116.6 (CH_3-C-CN).

3-O-Benzoyl-1,2-O-[1-(exo-cyano)ethylidene]-5,6-O-isopropylidene-α-D-galactofuranose 21. This was prepared from the corresponding 1,2-O-(1-methoxycarbonyl)ethylidene derivative 20 in 70% yield, m.p. 110-112° (from ether-hexane), R_f 0.50 (A), $[\alpha]_D$ +6° (c 1.0). ^{1}H-NMR: δ 6.24 (d, 1H, $J_{1,2}$ 4.2, H-1), 5.18 (bs, 1H, H-3), 5.01 (d, 1H, H-2), 4.30 (m, 2H, H-4,5), 4.05 (m, 1H, H-6a), 4.00 (m, 1H, H-6b), 1.90 (s, 3H, CH_3CCN), 1.54, 1.47 (2s, 2 x 3H, $(CH_3)_2C$). ^{13}C-NMR: δ 165.4 (PhCO), 106.85 (C-1), 89.1 (C-4), 85.8 (C-2), 77.2 (C-3), 75.4 (C-5), 66.0 (C-6), 26.8, 25.4, 110.4 ($(CH_3)_2C$), 24.7, 100.85, 116.4 (CH_3-C-CN).

O-(2-O-Acetyl-3-O-benzoyl-5,6-O-isopropylidene-β-D-galactofuranosyl)-(1-6)-O-(2,3,5-tri-O-benzoyl-β-galactofuranosyl)-(1-6)-3,5-di-O-benzoyl-1,2-O-[1-(exo-methoxycarbonyl)ethylidene]-α-D-galactofuranose 22. Glycosylation of the trityl ether 18 (2.44 g, 2.1 mmol) with CED 21 (0.79 g, 2.1 mmol) was carried out in dichloromethane (12 ml) in the presence of silver triflate (52 mg, 0.2 mmol) for 24 hr. The reaction mixture following quenching with pyridine (0.1 ml) was worked-up as described in the synthesis of 17 and chromatography then yielded 1.95 g (73%) of 22, R_f 0.45 (A), $[\alpha]_D$ -33°(c 0.8). ^{1}H-NMR: δ 6.19 (d, 1H, $J_{1,2}$ 3.8, H-1), 5.95 (m, 1H, H-5'), 5.66 (d, 1H, $J_{3,4}$ 1.5, H-3), 5.64 (m, 1H, H-5), 5.51 (bd, 1H, $J_{3,4}$ 3.3, H-3'), 5.50, 5.46 (2s, 2 x 1H, H-1',2'), 5.24 (dd, 1H, $J_{3,2}$ 0.8, $J_{3,4}$ 4.2, H-3"), 5.16 (s, 1H, H-1"), 5.10 (d, 1H, H-2"), 4.95 (d, 1H, H-2), 4.76 (dd, 1H, $J_{4,5}$ 4.8, H-4'), 4.72 (dd, 1H, $J_{4,5}$ 9.1, H-4), 4.40 (pq, 1H, H-5"), 4.32 (dd, 1H, $J_{4,5}$ 5.0, H-4"), 4.26 (dd, 1H, $J_{5,6a}$ 5.3, $J_{6a,6b}$ 10.9, H-6a), 4.12 (dd, 1H, $J_{5,6a}$ 4.5, $J_{6a,6b}$ 10.8, H-6a'), 4.05 (dd, 1H, $J_{5,6a}$ 6.5, $J_{6a,6b}$ 8.5, H-6a"), 4.00 (dd, 1H, $J_{5,6b}$ 7.5, H-6b'), 3.94 (m, 2H, H-6b,6b"), 3.76 (s, 3H, OCH_3), 2.02 (s, 3H, CH_3CO), 1.85 (s, 3H, CH_3C), 1.41, 1.36 (2s, 2 x 3H, $(CH_3)_2C$). ^{13}C-NMR: δ 169.5 (CH_3CO), 165.7 - 165.4 (PhCO), 107.2 (C-1), 106.3, 106.2 (C-1',1"), 86.2, 86.0 (C-2,4), 83.25, 82.4, 81.85, 81.3 (C-2',2",4',4"), 77.95, 77.3, 76.65, 75.35 (C-3,3', 3",5"), 71.7 x 2 (C-5,5'), 66.85, 66.2, 65.6 (C-6,6',6"), 26.3, 25.3, 109.9 ($(CH_3)_2C$), 21.4, 108.55, 52.6 (CH_3-C-$COOCH_3$), 20.7 (CH_3CO).

O-(2,3,5-Tri-O-benzoyl-6-O-trityl-β-D-galactofuranosyl)-(1-6)-O-(2,3,5-tri-O-benzoyl-β-D-galactofuranosyl)-(1-6)- 3,5-di-O-benzoyl-1,2-O-[1-(exo-cyano)ethylidene]-α-D-galactofuranose 23. To a soln of the derivative 22 (1.98 g, 1.5 mmol) in methanol (50 ml) was added catalytic amount of toluene-p-sulfonic acid and the mixture was stirred at 40°C until 22 was converted into a product with R_{22} 0.25 (A). The mixture was neutralised with pyridine and concentrated. Pyridine (20 ml) was added to, and distilled from, the residue which was then treated with triphenylchloromethane (550 mg, 2.0 mmol) in pyridine (10 ml) for 10 hr at 40°C. Conventional work-up followed by ammonolysis and treatment with benzoyl chloride afforded 23 which was isolated by HPLC in a yield of 1.40 g (57%), R_f 0.57 (A), $[\alpha]_D$ -24.5° (c 1.5). ^{1}H-NMR: δ 6.18 (d, 1H, $J_{1,2}$ 4.0, H-1), 5.99 (m, 1H, H-5"), 5.84 (m, 1H, H-5'),

5.72 (bs, 1H, H-3), 5.57 (bd, 1H, $J_{3,4}$ 4.2, H-3"), 5.55 (m, 1H, H-5), 5.53 (s, 1H, H-1'), 5.47 (bd, 1H, $J_{3,4}$ 5.0, H-3'), 5.42 (s, 1H, H-1"), 5.30 (s, 2H, H-2',2"), 4.91 (d, 1H, H-2), 4.85 (t, 1H, $J_{4,5}$ 3.9, H-4"), 4.73 (t, 1H, H-4'), 4.73 (bd, 1H, $J_{4,5}$ 9.1, H-4), 4.22 (dd, 1H, $J_{5,6a}$ 5.5, $J_{6a,6b}$ 10.5, H-6a), 4.13 (dd, 1H, $J_{5,6a}$ 4.5, $J_{6a,6b}$ 11.0, H-6a'), 4.03 (dd, 1H, $J_{5,6b}$ 7.2, H-6b'), 3.83 (dd, 1H, $J_{5,6b}$ 3.5, H-6b), 3.59 (dd, 1H, $J_{5,6a}$ 6.5, $J_{6a,6b}$ 9.8, H-6a"), 3.45 (dd, 1H, $J_{5,6b}$ 4.1, H-6b"), 1.98 (s, 3H, CH_3CCN). ^{13}C-NMR: δ 165.9 -165.2 (PhCO), 143,9 (Tr), 108.6, 108.3, 108.15 (C-1,1',1"), 86.8 (C-4), 85.5 (C-2), 82.4, 82.3, 81.73, 81.67 (C-2',2",4',4"), 77.95, 77.6 (C-3',3"), 76.1 (C-3), 72.15 (C-5"), 71.4, 71.2 (C-5,5'), 66.4 x 2 (C-6,6'), 62.9 (C-6"), 24.2, 108.6, 116.8 (CH_3-C-CN).

Cyclisation of the oligosaccharide monomers 2, 3, and 4. Cyclisation was carried out under conditions employed earlier [9] for polycondensation of the monomer 1. The monomers 2, 3, and 4 (amount is specified below) were treated with silver triflate (12.8 mg, 0.05 mmol) in dichloromethane (3 ml) at RT for 20 hr and the reaction mixtures were worked-up conventionally. From the dimer 2 (250 mg, 0.23 mmol) were obtained products with R_f 0.71, 0.53, and 0.20 (C), the trimer 3 (130 mg, 0.086 mmol) gave products with R_f 0.59 and 0.20 (C), and a product with R_f 0.53 (C) was obtained from the tetramer 4 (80 mg, 0.042 mmol). The thus obtained products were identified (with the previously synthesised[2] COS as standards) as cyclo-[(1-6)-2-O-acetyl-3,5-di-O-benzoyl-β-D-galactofurano]-biose 5, R_f 0.71, -triose 6, R_f 0.59, and -tetraose 7, R_f 0.53 (C).

Cyclisation of the disaccharide monomer 19 . Cyclisation of 19 (343 mg, 0.39 mmol) was carried out in dichloromethane (16 ml) in the presence of silver triflate (100 mg, 0.39 mmol) for 32 hr. Conventional work-up and column chromatography in a linear gradient of heptane-ethyl acetate (3:2 → 2:3) gave the dimer 31 (42 mg, 21%), tetramer 32 (41 mg, 20.5%), hexamer 33 (31 mg, 15.5%), and octamer 34 (24 mg, 12%).

31, R_f 0.76 (B), $[\alpha]_D$ -73° (c 1.45). ^{1}H-NMR: δ 5.69 (dd, 1H, $J_{2,1}$ 0.8, $J_{2,3}$ 3.7, H-2'), 5.64 (dd, 1H, $J_{3,4}$ 8.3, H-3'), 5.56 (m, 2H, H-5,5'), 5.50 (dd, 1H, $J_{2,1}$ 2.1, $J_{2,3}$ 4.5, H-2), 5.47 (dd, 1H, $J_{3,4}$ 8.3, H-3), 5.32 (bs, 1H, H-1'), 5.20 (bs, 1H, H-1), 4.60 (m, 2H, H-4,4'), 4.26 - 4.06 (m, 4H, H-6a,6b,6a',6b'), 2.10 (s, 3H, CH_3CO).

32, R_f 0.64 (B), $[\alpha]_D$ -60° (c 1.04). ^{1}H-NMR: δ 5.90 (m, 2H, H-5,5'), 5.50 (dd, 1H, $J_{3,2}$ 1.6, $J_{3,4}$ 5.0, H-3'), 5.49 (m, 2H, H-1',2'), 5.31 (dd, 1H, $J_{3,2}$ 1.8, $J_{3,4}$ 4.8, H-3), 5.26 (s, 1H, H-1), 5.18 (bs, 1H, H-2), 4.73 (dd, 1H, $J_{4,5}$ 1.6, H-4'), 4.68 (dd, 1H, $J_{4,5}$ 2.8, H-4), 4.21 - 3.93 (m, 4H, H-6a,6b,6a',6b'), 1.62 (s, 3H, CH_3CO).

33, R_f 0.57 (B), $[\alpha]_D$ -47° (c 1.2). ^{1}H-NMR: δ 5.86 (m, 2H, H-5,5'), 5.50 (bd, 1H, $J_{3,4}$ 5.0, H-3'), 5.34 (bd, 1H, $J_{2,3}$ 1.2, H-2'), 5.33 (s, 1H, H-1'), 5.32 (bd, 1H, $J_{3,4}$ 5.3, H-3), 5.22 (s, 1H, H-1), 5.14 (d, 1H, $J_{2,3}$ 1.0, H-2), 4.62 (m, 2H, H-4,4'), 4.15 - 3.95 (m, 4H, H-6a,6b,6a',6b'), 1.64 (s, 3H, CH_3CO).

34, R_f 0.50 (B), $[\alpha]_D$ -40° (c 1.0). ^{1}H-NMR: δ 5.87 (m, 2H, H-5,5'), 5.50 (bd, 1H, $J_{3,4}$ 4.6, H-3'), 5.32 (bd, 1H, $J_{3,4}$ 3.8, H-3), 5.31 (d, 1H, $J_{2,3}$ 1.0, H-2'), 5.28 (s, 1H, H-1'), 5.18 (s, 1H, H-1), 5.09 (d, 1H, $J_{2,3}$ 1.2, H-2), 4.61 (m, 2H, H-4,4'), 4.20 - 3.90 (m, 4H,

H-6a,6b,6a',6b'), 1.56 (s, 3H, CH_3CO).

Cyclo-[(1-6)-β-D-galactofurano]-biose 24, -tetraose 26, -hexaose 28, and -octaose 29. Deacylation of the protected COS 31 - 34 (20 - 40 mg) was performed with 0.1 M MeONa (5 -10 ml) in 4:1 chloroform - methanol mixture at RT with vigorous stirring for 4 hr. Following neutralisation with acetic acid and concentration the residues were dissolved in water (20 ml) and the solutions were washed with heptane (2 x 5 ml) and concentrated. Pure oligosaccharides were isolated by gel-chromatography : 24, R_f 0.61 (D), $[\alpha]_D$ -137° (c 2.2); 26, R_f 0.52 (D), $[\alpha]_D$ -113° (c 0.97); 28, R_f 0.36 (D), $[\alpha]_D$ -124° (c 1.04); 29, R_f 0.29 (D), $[\alpha]_D$ -90° (c 0.33). Chromatographic mobilities of the dimer 24 and tetramer 26 coincided with those of COS prepared by deacylation of 5 and 7, respectively.

Cyclisation of the trisaccharide monomer 23. The monomer 23 (1.073 g, 0.66 mmol) was treated with silver triflate (180 mg, 0.7 mmol) in dichloromethane (30 ml). After 42 hr at RT pyridine (1 ml) was added and the reaction mixture was processed as above. Isolated by gel-chromatography were the trimer 25 (25.7 mg, 24%), R_f 0.56 (D), $[\alpha]_D$ -78° (c 1.2), hexamer 28 (25.2 mg, 23.6%), R_f 0.36 (D), $[\alpha]_D$ -118° (c 1.0), and nonamer 30 (18.2 mg, 17%), R_f 0.15 (D), $[\alpha]_D$ -129° (c 0.74).

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