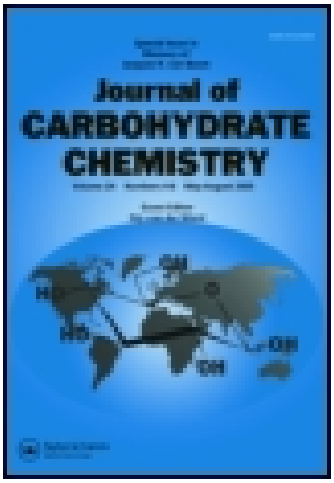

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Regioselective Synthesis of Partially Protected Trehalose Analogues and Assignment of Ring Size in Isopropylidene Acetal Derivatives by ^{13}C Nmr Spectroscopy

Rafik W. Bassily [a], Rimon H Youssef [a], Ramadan I. El-Sokkary [a] & Mina A Nashed [a]

[a] Department of Chemistry, Faculty of Science Alexandria University, Ebrahemia, P.O. Box 426, Alexandria, 21321, EGYPT

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REGIOSELECTIVE SYNTHESIS OF PARTIALLY PROTECTED TREHALOSE ANALOGUES AND ASSIGNMENT OF RING SIZE IN ISOPROPYLIDENE ACETAL DERIVATIVES BY ^{13}C NMR SPECTROSCOPY

Rafik W. Bassily, Rimon H. Youssef, Ramadan I. El-Sokkary and Mina A. Nashed*

Department of Chemistry, Faculty of Science, Alexandria University, Ebrahemia P.O. Box 426, Alexandria 21321 (EGYPT)

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ABSTRACT

The ^{13}C NMR spectra of a range of di-*O*-isopropylidene acetals of α,α-trehalose and its analogues **1, 2, 4-7** have been studied. Attention has been focussed on the chemical shifts of the acetal carbon and methyl groups of the acetals. These parameters are characteristic of ring-size (1,3-dioxolane and 1,3-dioxane). Di-*n*-butylstannylene and cyclic orthoester intermediates **9** and **12** of 2,6-di-*O*-benzoyl-α-D-galactopyranosyl 2,6-di-*O*-benzoyl-α-D-galactopyranoside (**8**) were used to synthesize the partially protected trehalose analogue having chain extension at positions 4,4' and 3,3' (**10** and **13**) respectively. Acetonation of the synthetic trehalose type disaccharide yielded mainly 3,4:3',4'-di-*O*-isopropylidene derivative **4**. The benzoylation of **4** followed by acid hydrolysis gave **8** in 85% yield, which was the key intermediate for the synthesis of **10** and **13**.

INTRODUCTION

α,α-Trehalose is widely distributed in Nature and plays an important role as an energy source as well as a carbohydrate reserve in insects.[1] To help the biochemical investigation of the metabolism and the functions of α,α-trehalose, a domain of research attracting much current interest,[2-5] a large assortment of modified derivatives of this disaccharide is required.[6,7]

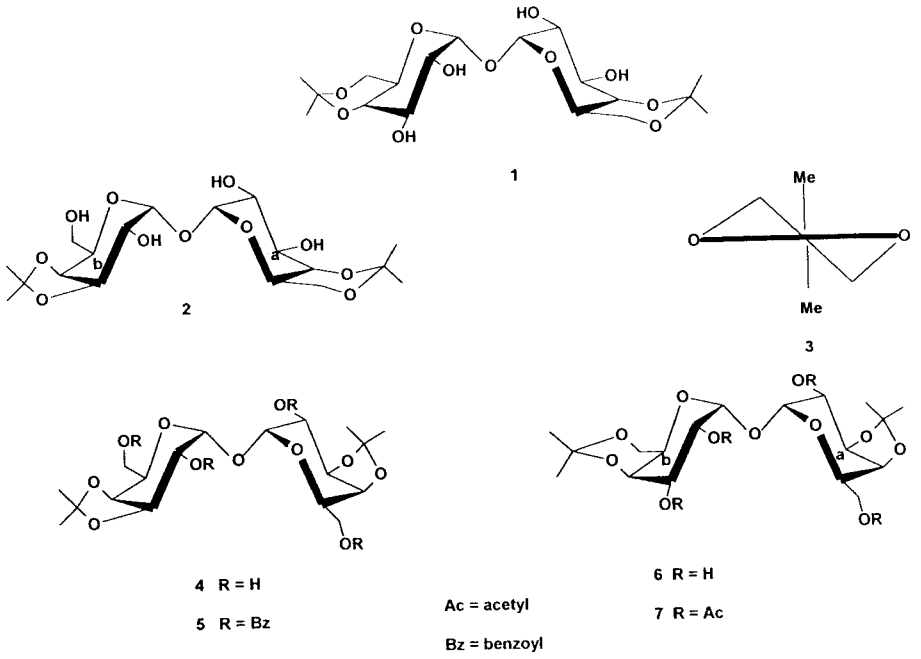
Isopropylidene groups, in the form of cyclic acetals, are used in carbohydrate chemistry for the specific protection of diol functions.[8] In addition to their practical value there has been interest in the structures themselves especially their conformational analysis,[9-11] and the factors leading to the formation of particular ring sizes when more than one is possible.[12]

A most useful route for obtaining a single free secondary hydroxyl group in a pyranoside, adjacent to an axial one is to prepare a cyclic orthoester and then open this under mild acidic conditions. The opening is regioselective and leaves the acyl group in the axial position.[13] The opposite substitution pattern is obtained by the acylation or alkylation of the stannylene derivatives of pyranoside[14-17] or true cyclohexane derivatives[14] having an axial-equatorial diol when the reaction is performed in the presence of an added nucleophile or base.[18]

We now report the use of these strategies on α-D-galactopyranosyl α-D-galactopyranoside.[19] Moreover, we studied the assignment of ring size in di-*O*-isopropylidene acetals of α,α-trehalose and its analogues by ^{13}C NMR spectroscopy.

RESULTS AND DISCUSSION

Assignment of ring size in di-O-isopropylidene acetals of α,α-trehalose and its analogues by ^{13}C NMR spectroscopy. The direct acetonation of α,α-trehalose and its analogues, which were synthesized by a facile method,[7,19] with a mixture of 2,2-dimethoxypropane and acetone in DMF containing a catalytic amount of *p*-toluenesulfonic acid at 50 °C afforded **1**, **2**, **4** and **6**.



Scheme 1

The ^{13}C NMR spectrum of 4,6:4',6'-di-*O*-isopropylidene-α,α-trehalose (**1**) showed the acetal carbon atom at δ 99.09 (Table 1), in which the 1,3-dioxane ring is *trans*-fused to a pyranoid ring. Moreover, the signals due to the 1,3-dioxane methyl groups are widely separated (Δδ = 9.99 ppm) (Table 1). This pattern is due to an axial methyl (higher field) and equatorial methyl (lower field),[20] and is a clear indication that the dioxane ring has a chair conformation.[21,22]

Isopropylidenation of α-D-galactopyranosyl α-D-glucopyranoside[7] gave 3,4-*O*-isopropylidene-α-D-galactopyranosyl 4,6-*O*-isopropylidene-α-D-glucopyranoside (**2**). Characterization of compound **2** was based on its ^{13}C NMR spectrum, in which the two signals at δ 108.19 and 99.19 (Table 1) were due to the acetal carbon atom in 1,3-dioxolane ring and 1,3-dioxane ring, respectively. Furthermore, the signals attributed to the dioxane methyl groups appear at δ 29.38 and 19.43, while in the dioxolane ring the methyl groups appear at δ 28.68 and 26.76. It is likely that the small difference in the chemical shift is due to the flexibility of the 1,3-dioxolane ring[23,24] and the similarity of the

TABLE 1

^{13}C-Chemical Shifts for Di-*O*-Isopropylidenes Trehalose Type Disaccharides

Compound	1,3-Dioxane ring			1,3-Dioxolane ring		
	Acetal carbon	Methyl carbons	Δδ(Methyl carbons)	Acetal carbon	Methyl carbons	Δδ(Methyl carbons)
1[a]	99.09	19.50, 29.49	9.99	—	—	—
2[a]	99.19	19.43, 29.38	9.95	108.19	26.76, 28.68	1.92
4[a]	—	—	—	107.71	26.26, 28.16	1.90
5[b]	—	—	—	110.99	26.90, 28.41	1.51
6[a]	97.63	16.71, 27.61	10.90	107.92	24.52, 26.55	2.03
7[b]	98.98	18.47, 29.24	10.77	110.31	26.25, 27.62	1.37

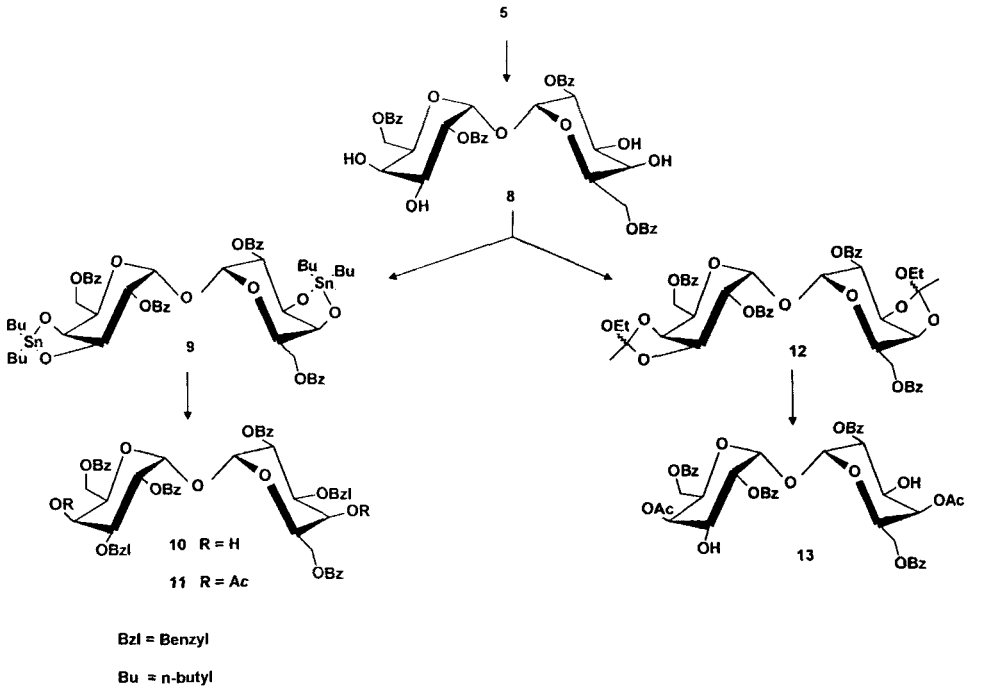
a. Determined in $(CD_3)_2SO$ with Me_4Si as the internal standard.

b. Determined in $CDCl_3$ with Me_4Si as the internal standard.

environment of the two methyl groups. The most probable conformation[25] of the 2,2-dimethyl-1,3-dioxolane ring is $^5T_4$ (**3**) in which the two methyl groups are equivalent.

The cyclic diacetals formed from α-D-galactopyranosyl α-D-galacto- pyranoside[19] furnished a 5:1 mixture of the thermodynamically more stable 3,4:3',4'-diacetal **4** and the kinetically favored 3,4:4',6'-diacetal **6**, which were isolated by chromatography on a silica gel column. The structures of these compounds were assigned by ^{1}H and ^{13}C NMR spectroscopy (Table 1). Moreover, the structure of the non-symmetrical diacetals **6** was confirmed from the ^{1}H NMR spectrum of its per-*O*- acetyl derivative **7**, which showed a doublet of doublets at δ 5.21 with splittings of 10.9 and 3.5 Hz, identifiable by a 2D ^{1}H-^{1}H correlation experiment (COSY) as the signal for H-3b, indicating that an *O*-acetyl group was located at this position.

Regioselective synthesis of partially protected trehalose analogues. Benzoylation of compound **4** afforded the tetra-*O*-benzoyl derivative **5** in 85% yield. The characterization of compound **5** was based on its ^{1}H NMR spectrum, in which the signal for H-2 had a small ($J_{1,2}$= 3.7 Hz) and a large ($J_{2,3}$= 7.8 Hz) coupling and the resonances



Scheme 2

due to H-3 appeared as a doublet of doublets ($J_{2,3}$=7.8 Hz, $J_{3,4}$= 5.6 Hz). It is evident, primarily from these values, that a major change from $^4C_1$(D) conformation accompanies the *cis*-fusion of 1,3-dioxolane ring.

Treatment of **5** with 80% acetic acid furnished 2,6-di-*O*-benzoyl-α-D-galactopyranosyl 2,6-di-*O*-benzoyl-α-D-galactopyranoside (**8**) in good yield. The structure of **8** was confirmed from ^{1}H and ^{13}C NMR spectra, in which the signals of isopropylidene moiety were not present, and the J values of the vicinal couplings of H-2 and H-3 were in the normal range.

Treatment of compound **8** with 2.4 equiv of dibutyltin oxide in boiling methanol[14-17] gave the unstable 3,4:3',4'-di-*O*-dibutylstannylene derivative **9**, which was immediately treated with benzyl bromide and tetrabutylammonium bromide[26,27] in dry benzene to give **10** (83%). Characterization of compound **10** was based on the ^{1}H NMR spectrum of its acetyl derivative **11**, in which the signal for H-4 showed a broadened doublet (J=3.2 Hz)

at δ 5.50. This proved that the parent alcohol **10** had a free hydroxyl groups at C-4,4'; conversely, a downfield shift of the signal of the H-3 was not observed.

The regioselective acetylation of the axial *O*-4,4' in **8** was accomplished by the formation of its cyclic orthoester derivative **12**. Compound **12**, without purification, was treated with 80% acetic acid at ambient temperature to afford the 4,4'-di-*O*-acetyl derivative **13** in 68% yield. The ^{1}H NMR spectrum of **13** showed a downshifted broad doublet (δ 5.45) due to H-4.

EXPERIMENTAL

General methods. Melting points were measured with a Gallen-kamp melting point apparatus and are uncorrected. Optical rotation were determined at 22 °C with a Perkin-Elmer Model 241 polarimeter. ^{1}H NMR spectra were recorded at Glycomed, Inc. with a Varian Gemini 300 MHz spectrometer at ambient temperature, and ^{13}C NMR spectra with a Varian Gemini 300 MHz instrument operating at 75.50 MHz. Chemical shifts are referenced to Me_4Si as the internal standard and the assignments of ^{13}C peaks were supported by attached proton test experiments (APT), and carbon-proton shift correlation experiments. Liquid secondary ion mass spectrometry (LSIMS) was performed on a Finnigan MATTSQ-70, triple-stage quadrupole mass spectrometer equipped with an Antek cesium ion gun. Glycerol or 3-nitrobenzyl alcohol (m-NBA, Aldrich) was employed as the sample matrix. Separations were accomplished by open-column chromatography on Merck silica gel 60 (70-230 mesh). TLC was performed on silica gel plates (250 μm, Merck). The following solvent combinations (v/v) were utilized for thin-layer and column chromatography: A, 9:1 $CHCl_3$-MeOH; B, 19:1 $CHCl_3$-MeOH; C, 9:1 toluene- EtOAc; D, 3:1 toluene-EtOAc; E, 19:1 $CHCl_3$-acetone. Elemental analyses were performed at the Galbraith Laboratories, Inc., Knoxville, TN 37821.

3,4-*O*-Isopropylidene-α-D-galactopyranosyl 3,4-*O*-isopropylidene-α-D-galactopyranoside (4). To a solution of α-D-galactopyranosyl α-D-galactopyranoside[19,28] (0.90 g, 2.6 mmol) in dry DMF (15 mL), absolute acetone (15 mL), and 2,2-dimethoxypropane (15 mL) together with *p*-toluenesulfonic acid (25 mg, 0.13 mmol)

were added. The reaction mixture was stirred for 30 min at 50 °C, at which time TLC (solvent A) showed the disappearance of the starting material. Triethylamine (0.3 mL, 2.2 mmol) was added, and the mixture was stirred for 15 min, the solvents were evaporated to dryness and coevaporated with toluene to remove traces of triethylamine. A solution of the crude product in 10:1 MeOH-H_2O (50 mL) was boiled under reflux for 3 h. After this period, TLC (solvent A) revealed a faster-moving major component and slower-moving minor component. The solvents were evaporated and the residue was chromatographed on a column of silica gel (solvent B) to separate, first, compound **4** (0.84 g, 76%) as an amorphous solid; $[\alpha]_D$ + 173°, $[\alpha]_{436}$ + 338° (*c* 0.6, MeOH); ^{1}H NMR (DMSO-d_6) δ 1.26, 1.40 [2s, 6H, (Me_2C)], 3.35-3.60, 4.11-4.18 (2m, 6H, sugar CH and CH_2), 4.72(bt, 1H, D_2O-exchangeable, OH-6), 4.87(d, 1H, $J_{1,2}$ = 3.4 Hz, H-1) and 4.96 (d, 1H, J= 7.6 Hz, D_2O-exchangeable, OH-2); ^{13}C NMR (DMSO-d_6) δ 26.26, 28.16(Me_2 C), 60.29 (C-6), 68.19, 69.09, 72.85, 75.59, 92.50(C-1) and 107.71 (CMe_2); positive-ion LSIMS: *m/z* 423.4 $(M+H^+)$, 445.4 $(M+Na)^+$, negative-ion LSIMS: *m/z* 421.4 $(M-H^+)^-$.

Anal. Calcd for $C_{18}H_{30}O_{11}$ (422.42): C, 51.18; H, 7.16. Found: C, 50.92; H, 7.50.

Eluted second was the minor component 4,6-*O*-isopropylidene-α-D-galactopyranosyl 3,4-*O*-isopropylidene-α-D-galactopyranoside (**6**), which was crystallized from acetone as fine needles (160 mg, 14%): mp 220-222 °C; $[\alpha]_D$ + 180°, $[\alpha]_{436}$ + 353° (*c* 1.8, MeOH); ^{1}H NMR (DMSO-d_6) δ 1.32, 1.38, 1.48, 1.49 [4s, 12H, 2(Me_2C)], 3.63-4.48 (m, 16H, sugar CH, CH_2, and 4 OH), 5.03 (d, 1H, $J_{1,2}$= 3.6 Hz, H-1a or 1b) and 5.15 (d, 1H, $J_{1,2}$= 3.4 Hz, H-1a or 1b); ^{13}C NMR (DMSO-d_6) δ 16.71, 27.61 (Me_2C)b, 24.52, 26.55 (Me_2C)a, 60.39, 61.41 (C-6a,6b), 61.99 (C-4b), 66.97, 67.23, 67.71, 68.37, 69.04, 72.73, 75.17, 92.51, 93.70 (C-1a,1b), 97.63 (CMe_2)b and 107.92 (CMe_2)a; negative-ion LSIMS: *m/z* 421.2 $(M-H^+)^-$.

Anal. Calcd for $C_{18}H_{30}O_{11}$ (422.42): C, 51.18; H, 7.16. Found: C, 51.25; H, 7.18.

2,3-Di-*O*-acetyl-4,6-*O*-isopropylidene-α-D-galactopyranosyl 2,6-di-*O*-acetyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (7). Acetylation of **6** with acetic anhydride in pyridine afforded the title compound 7 as a syrup in almost quantitative yield;

$[\alpha]_D$ + 145°, $[\alpha]_{436}$ + 287° (*c* 1.9, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.34-1.54 [4s, 12H, 2(Me_2C)], 2.08-2.12 (4s, 12H, OAc), 3.73 (bs, 1H, H-5b) 3.93 (dq, 2H, J= 12.9 Hz, H-6,6'b), 4.23-4.34 (m, 4H, H-4a, H-5a, H-6,6'a), 4.39 (dd, 1H, $J_{3,4}$= 5.4 Hz, H-3a), 4.45 (d, 1H, $J_{3,4}$= 3.4 Hz, H-4b), 5.07 (dd, 1H, $J_{2,3}$= 7.8 Hz, H-2a), 5.19 (d, 1H, $J_{1,2}$= 3.7 Hz, H-1a), 5.21 (dd, 1H, $J_{3,4}$= 3.5 Hz, H-3b), 5.34 (d, 1H, $J_{1,2}$= 3.6 Hz, H-1b) and 5.42 (dd, 1H, $J_{2,3}$= 10.9 Hz, H-2b); ^{13}C NMR ($CDCl_3$) δ 20.64, 20.77, 20.82, 20.97, ($4CH_3CO$), 26.25, 27.62, (Me_2C)a, 18.47, 29.24, (Me_2C)b, 62.25 (C-6 a or b), 62.70 (C-4b), 63.37 (C-6 a or b), 66.66, 66.87, 67.14, 68.31, 70.42, 73.05, 73.25, 92.39, 93.47 (C-1a,1b),98.98 (CMe_2)b, 110.31 (CMe_2)a and 169.65, 169.85, 170.67, 170.80 ($4COCH_3$); positive-ion LSIMS: *m/z* 591.0 $(M+H^+)$, 613.1 $(M+Na)^+$.

Anal. Calcd for $C_{26}H_{38}O_{15}$ (590.56): C, 52.88; H, 6.49. Found: C, 53.12; H, 6.68.

2,6-Di-*O*-benzoyl-3,4-*O*-isopropylidene-α-D-galactopyranosyl 2,6-di-*O*-benzoyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (5). To a solution of compound **4** (290 mg, 0.69 mmol) in pyridine (5 mL), benzoyl chloride (0.5 mL, 4.3 mmol) was added. The reaction mixture was stirred overnight at ambient temperature, after this period, TLC (solvent C) showed complete reaction. The mixture was poured into cooled 5% HCl, then extracted with CH_2Cl_2 and the extract was washed successively with $NaHCO_3$ solution and water, dried, and concentrated. The resultant syrup was crystallized from EtOH-ether as needles (490 mg, 85%): mp 141-142 °C; $[\alpha]_D$+107°, $[\alpha]_{436}$ + 209° (*c* 0.73, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.35, 1.55 [2s, 6H, (Me_2C)], 4.16-4.39 (m, 4H, sugar CH and CH_2), 4.58 (dd, 1H, $J_{3,4}$= 5.6 Hz, H-3), 5.33 (dd, 1H, $J_{2,3}$= 7.8 Hz, H-2),5.48 (d, 1H, $J_{1,2}$= 3.7 Hz, H-1) and 7.25-7.90 (m, 10H, H_{Ar}); ^{13}C NMR ($CDCl_3$) δ 26.90, 28.41 (Me_2C), 63.98 (C-6), 67.14, 71.61, 73.84, 73.89, 91.86 (C-1), 110.99 (CMe_2), 128.00-133.50 (aromatic carbons) and 165.00, 165.50 (2COPh); positive-ion LSIMS: *m/z* 839.0 $(M+H^+)$, 861.0 $(M+Na)^+$; negative-ion LSIMS: *m/z* 991.6 (M+m-NBA)$^-$.

Anal. Calcd for $C_{46}H_{46}O_{15}$ (838.83): C, 65.86; H, 5.53. Found: C, 66.12; H, 5.74.

2,6-Di-*O*-benzoyl-α-D-galactopyranosyl 2,6-di-*O*-benzoyl-α-D-galactopyranoside (8). Pure **5** (400 mg, 0.48 mmol) was dissolved in 80% aqueous acetic acid (10 ml), the solution was heated at 90 °C, and the reaction was monitored by TLC (solvent A). Heating was discontinued as soon as hydrolysis was complete (1h), as

prolongation of the reaction time was found to decrease the yield of product. The mixture was concentrated to dryness under diminished pressure, and then coevaporated with toluene. The residue was purified on a column of silica gel (solvent B) that furnished an amorphous solid **8** (310 mg, 85%): $[\alpha]_D$ + 114°, $[\alpha]_{436}$ + 217°(*c* 0.74, CH_2Cl_2); ^1H NMR (DMSO-d_6 + D_2O) δ 3.92-4.32 (m, 5H, sugar CH and CH_2) 5.46 (dd, 1H, $J_{2,3}$= 10.2 Hz, H-2), 5.53 (d, 1H, $J_{1,2}$= 3.8 Hz, H-1) and 7.25-8.00 (m, 10H, H_{Ar}); ^{13}C NMR (DMSO-d_6) δ 63.29 (C-6), 66.58, 68.79, 68.97, 70.61, 90.81 (C-1), 128.00-133.50 (aromatic carbons) and 165.00, 165.50 (2COPh).

Anal. Calcd for $C_{40}H_{38}O_{15}$ (758.70):C, 63.32; H, 5.05. Found: C, 62.96; H, 5.31.

4-*O*-Acetyl-2,6-di-*O*-benzoyl-3-*O*-benzyl-α-D-galactopyranosyl 4-*O*-acetyl-2,6-di-*O*-benzoyl-3-*O*-benzyl-α-D-galactopyranoside (11). A stirred mixture of **8** (190 mg, 0.25 mmol) and dibutyltin oxide (150 mg, 2.4 molar equiv) in MeOH (10 mL) was heated for 1 h under reflux. The MeOH was evaporated off and the residual solid was dried under vacuum for 2 h and then used as such. No satisfactory way of monitoring the progress of the reaction was found, but the subsequent behavior of the syrup demonstrated that it was the desired di-*n*-butylstannylene derivative **9**. Compound **9** was dissolved in dry benzene (5 mL), benzyl bromide (0.5 mL, 4.2 mmol), and tetrabutylammonium bromide (100 mg, 0.31 mmol) were added. The reaction mixture was heated for 24 h at 75-80 °C, at which time, TLC (solvent D) showed no starting material and only one major product spot. The solution was concentrated to dryness, and the residue was purified on a column of silica gel (solvent C) to afford **10** (195 mg, 83%) as a syrup. Acetylation of **10** (195 mg, 0.21 mmol) with acetic anhydride (2 mL) in pyridine (4 mL) furnished the title compound **11** in almost quantitative yield as a syrup: $[\alpha]_D$ + 152°, $[\alpha]_{436}$ + 304° (*c* 0.88, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.13 (s, 3H, OAc), 3.83-4.12 (m, 4H, sugar CH and CH_2), 4.52, 4.72 (AB, 2H, J = 12.0 Hz, $PhCH_2$), 5.45 (dd, 1H, $J_{2,3}$=10.3 Hz, H-2), 5.50 (d, 1H, J=3.2 Hz, H-1 or H-4), 5.53 (d, 1H, J=3.7 Hz, H-1 or H-4) and 7.20-7.90 (m, 15H, H_{Ar}); decoupling: δ 5.45 (dd, 1H, $J_{2,3}$= 10.3 Hz; → d, $J_{1,2}$= 3.7 Hz on irradiation at 4.06, H-2), 5.50 (d, 1H, $J_{3,4}$= 3.2 Hz; → s, on irradiation at 4.06, H-4) and 5.53 (d, 1H, $J_{1,2}$ = 3.7 Hz; → s, on irradiation at 5.45, H-1); ^{13}C NMR ($CDCl_3$) δ 21.36 (CH_3CO), 62.52 (C-6), 67.46 (C-4), 68.03 (C-5), 70.17 (C-2), 72.31 ($PhCH_2$),

73.30 (C-3), 92.59 (C-1), 128.00-138.00 (aromatic carbons), 165.50, 166.00 (2COPh) and 171.00 ($COCH_3$).

Anal. Calcd for $C_{58}H_{54}O_{17}$ (1023.01): C, 68.09; H, 5.32. Found: C, 67.88; H, 5.46.

4-*O*-Acetyl-2,6-di-*O*-benzoyl-α-D-galactopyranosyl 4-*O*-acetyl-2,6-di-*O*-benzoyl-α-D-galactopyransoide (13). To a solution of compound **8** (0.6 g, 0.79 mmol) in dry benzene (7 mL), triethyl orthoacetate (0.5 mL, 2.73 mmol), and *p*-toluenesulfonic acid monohydrate (10 mg) were added. The reaction mixture was stirred for 1 h at ambient temperature, after which TLC (solvent D) showed complete reaction. Triethylamine (0.1 mL) was added, and the mixture was stirred for 15 min. The mixture was concentrated to dryness and coevaporated with toluene to remove traces of triethylamine. The crude orthoester derivative **12** was dissolved in 80% aqueous acetic acid (5 mL), and the solution was kept at room temperature for 10 min. After this period, TLC (solvent E) indicated complete conversion of **12** into the less mobile **13**. Evaporation of the solvent under diminished pressure left a crude syrup, which was purified by chromatography on silica gel (solvent D) to give **13** (450 mg, 68%) as a syrup: ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 3H, OAc) 3.90-4.14 (m, 3H, 1 OH, and sugar CH_2), 4.26 (bt, 1H, H-5), 4.54 (dd, 1H, $J_{3,4}$= 3.5 Hz, H-3), 5.40 (dd, 1H, $J_{2,3}$= 10.4 Hz, H-2), 5.45 (d, 1H, $J_{3,4}$= 3.3 Hz, H-4), 5.57 (d, 1H, $J_{1,2}$= 3.7 Hz, H-1) and 7.20-8.10 (m, 10H, H$_{Ar}$); ^{13}C NMR ($CDCl_3$) δ 21.34 (CH_3CO), 62.28 (C-6), 67.58, 68.07, 70.90, 71.54, 92.78 (C-1), 129.00-134.00 (aromatic carbons), 166.00, 166.75 (2COPh) and 171.75 ($COCH_3$); negative-ion LSIMS: *m/z* 995.4 (M + m-NBA)$^-$.

Anal. Calcd for $C_{44}H_{42}O_{17}$ (842.78): C, 62.70; H, 5.02. Found: C, 62.74; H, 5.15.

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