SOME STANNYLATED GALACTOSE DERIVATIVES

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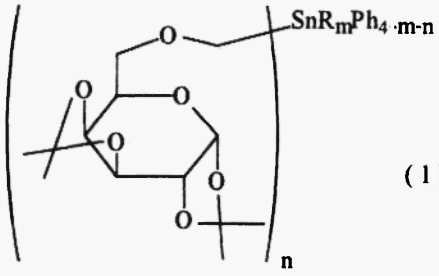
ABSTRACT.

The synthesis and NMR spectra of 1,2:3,4-di-*O*-isopropylidene-6-*O*-[(3-triphenylstannyl)propyl]-α-D-galactopyranose (**4**), 3-(triphenylstannyl)propyl α-D-galactopyranoside (**6**), obtained by hydrostannation of 6-*O*-allyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**3**) and allyl α-D-galactopyranoside (**5**), respectively, and 1,6-anhydro-3,4-*O*-isopropylidene-2-*O*-[(triphenyl-stannyl)methyl]-β-D-galactopyranose (**8**), produced from Ph_3SnCH_2I and 1,6-anhydro-3,4-*O*-isopropylidene-β-D-galactopyranose (**7**), are reported. The solution conformations of the carbohydrate rings in **4**, **6**, and **8** are similar to those in the non-stannylated precursor molecules, **3**, **5** and **7**. Furthermore, an X-ray diffraction study of **8** indicated a similar carbohydrate core structure to that found for solid **7**: the tin centre in **8** has a tetrahedral geometry. Both the mono-iodotin derivatives, 1,6-anhydro-2-*O*-[(iododiphenylstannyl)methyl]-3,4-*O*-isopropylidene-β-D-galacto-pyranose (**12**), and [3-(iododiphenylstannyl)propyl] α-D-galactopyranoside (**11**) are 4-coordinate species in solution; in contrast, 6-*O*-[3-(iodo-diphenylstannyl)propyl]-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**9**) is a 5-coordinate species in $CDCl_3$ solution. The sugar unit in **9** is thus a more effective chelating ligand than are either of the sugar units in **11** and **12**.

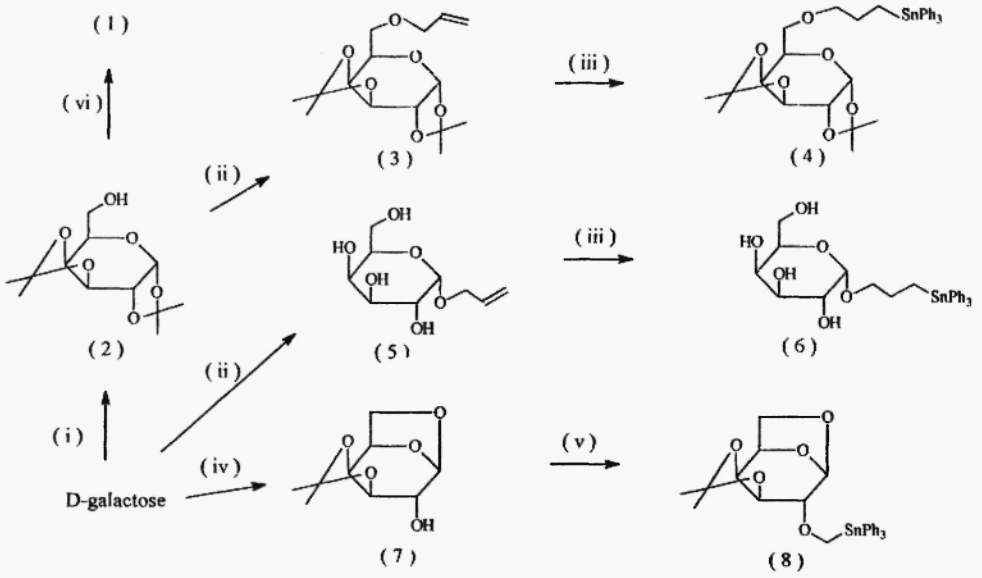
INTRODUCTION.

We recently reported[1] the synthesis and NMR spectra of a family of 6-*O*-[(1,2:3,4-di-*O*-isopropylidene)-α-D-galactopyranosyl)]methyl-tin compounds, (**1**). The crystal structure of one member of this series, (**1**; n = 1, m = 0)[2], has been determined, as has that of the monoiodo species, (**1**; m = 1, n = 2, R = I)[1]. These mono-, di- and tri-saccharide derivatives, (**1**), were obtained *via* the reactions of appropiate iodomethyltin reagents with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, (**2**).



(**1**) m = 0; n = 1-3
m = 1-3; n = 1; R = Me
m = 3; n = 1; R = Bu

In continuation of a study of stannylated carbohydrate species, we have investigated other galactopyranose species, in which the position and/or separation of the organotin moiety with respect to the pyranose ring is varied, as shown in Scheme 1.



SCHEME 1: Reagents (i) Me_2CO, $ZnCl_2$; (ii) NaH, $H_2C{=}CHCH_2Br$; (iii) Ph_3SnH, AIBN ; (iv) moist Me_2CO, $ZnCl_2$; (v) Ph_3SnCH_2I ; (vi) $R_mPh_{4-m-n}Sn(CH_2I)_n$

EXPERIMENTAL.

IR spectra were recorded on a Philips Analytical PU9800 Fourier-transform spectrometer. Solution NMR spectra were obtained on a Bruker 250 MHz instrument. The conventional carbohydrate numbering system has been used for the NMR spectral data for the sugar rings; the numbering system used for the allylic ethers and for the stannylpropyloxy moieties are:

$$\underset{(9)\ (8)\ (7)}{H_2C{=}CH{-}CH_2{-}O-} \quad \text{and} \quad \underset{(9)\ (8)\ (7)}{R_2R'SnCH_2{-}CH_2{-}CH_2{-}O-}$$

Triphenyltin hydride[3] and (iodomethyl)triphenyltin[1] were prepared by published procedures.

6-O-Allyl-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (3).

A modification to a published procedure was adopted.[4] Excess NaH (5 g) was added to a solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, (**2**) (10.20 g, 39 mmol), and allyl bromide (14.22 g, 118 mmol) in dry DMF (50 ml). After the reaction was complete (as shown by TLC), water (50 ml) and ether (50 ml) were successively added. The organic phase was collected and the aqueous phase extracted with ether (2 x 50 ml). The combined ethereal solutions were washed with water (2 x 50 ml), dried over magnesium

sulphate and rotary evaporated. The title compound (**3**) was obtained on distillation; b.p. 76-78 °C/ 0.001 mm Hg (lit.[4] value 110 °C/ 0.06 mm Hg).

Analysis found: C, 59.7; H, 8.2%. $C_{15}H_{24}O_6$ requires C, 60.0; H, 8.1%.

IR (cm^{-1}) : 3077, 2986, 2928, 1647, 1458, 1381, 1372, 1256, 1211, 1169, 1109, 1070, 1005, 959, 918, 866.

^1H NMR (250 MHz, $CDCl_3$) δ :1.31 [s, 3H, Me], 1.33 [s, 3H, Me], 1.43 [s, 3H, Me], 1.53 [s, 3H, Me], 3.56 [dd, 1H, H_6, J = 6.8 & 10.1 Hz), 3.64 [dd, 1H, H_6, J = 5.8 & 10.1 Hz], 3.96 [ddd, 1H, H_5, J = 1.8, 5.8 & 6.8 Hz], 4.03 [ddd, 2H, H_7, J = 1.3, 1.5 & 5.6 Hz], 4.25 [dd, 1H, H_4, J = 1.8 & 7.9 Hz], 4.29 [dd, 1H, H_2, J = 2.4 & 5.0 Hz], 4.58 [dd, 1H, H_3, J = 2.4 & 7.9 Hz], 5.16 [ddd, 1H, H_9, J =1.3, 1.6 & 10.4 Hz], 5.27 [dddd, 1H, H_9, J =1.5, 1.5, 1.6 & 18 Hz], 5.52 [d, 1H, H_1, J = 5.0 Hz], 5.90 [dddd, 1H, H_8, J = 5.6, 5.6, 10.4 & 18Hz].

^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 24.4 [Me], 24.9 [Me], 25.9 [Me], 26.0 [Me], 66.7 [C_5], 68.7 [C_6], 70.5 [C_2], 70.6 [C_3], 71.1 [C_4], 72.2 [C_7], 96.3 [C_1], 108.4, 109.1 [2 CMe_2], 117.0 [C_9], 134.7 [C_8].

1,2:3,4-Di-O-isopropylidene-6-O-[(3-triphenylstannyl)propyl]-α-D-galactopyranose (4).

A mixture of **3**, (2.0 mmol), Ph_3SnH (10 mmol) and a catalytic quantity of AIBN was refluxed in benzene (5 ml). TLC [irrigant: petrol (60-80 °C) : ethyl acetate] was used to monitor the reaction. The residue, after rotary evaporation of the product mixture, was dissolved in ether and filtered to remove Ph_3SnH hydrolysis products. The filtrate was rotary evaporated and the residue purified using the chromatotron, using petrol: ethyl acetate (9:1 v/v) as eluant. The pure product was obtained in a yield of 86% as an oil.

Analysis found: C, 61.3; H, 6.2%. $C_{33}H_{40}O_6Sn$ requires: C, 60.9; H, 6.2%.

IR (cm^{-1}): 3063, 3046, 2986, 2930, 1482, 1456, 1429, 1379, 1375, 1256, 1211, 1171, 1071, 1003, 918, 893, 862, 729, 700, 511, 448.

^1H NMR (250 MHz, $CDCl_3$) δ: 1.38 [s, 6H, 2Me], 1.50 [s, 3H, Me], 1.56 [s, 3H, Me]), 1.53-1.62 [m, 2H, H_9], 2.02-2.14 [m, 2H, H_8], 3.54 [ddd, 1H, H_7, J = 6.4, 6.4 & 9.4 Hz], 3.56 [dd, 1H, H_6, J = 6.5 & 10.2 Hz], 3.56-3.65 [ddd, 1H, H_7', J = 6.5, 6.5 & 9.4 Hz], 3.63 [dd, 1H, H_6', J = 5.8 & 10.2 Hz], 3.98 [ddd, 1H, H_5, J = 1.8 , 5.8 & 6.5 Hz], 4.22 [dd, 1H, H_4, J = 1.8 & 7.9 Hz], 4.36 [dd, 1H, H_2, J = 2.4 & 5.0 Hz], 4.64 [dd, 1H, H_3, J = 2.4 & 7.9 Hz], 5.60 [d, 1H, H_1, J =5.0 Hz], 7.39 [m, 9H, *m*- + *p*-aryl-H], 7.58-7.66 [m, 6H, *o*-aryl-H, $J(^{119,117}Sn\text{-}^1H)$ = 45 Hz].

^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 6.89 [C_9, $J(^{119/117}Sn\text{-}^{13}C)$ = 398/382 Hz], 24.4, 24.9, 25.9, 26.0 [4x CH_3], 26.4 [C_8, $J(^{119,117}Sn\text{-}^{13}C)$ = 20 Hz], 66.6 [C_5], 70.5 [C_2], 70.6 [C_3], 71.1 [C_4], 74.1 [C_7, $J(^{119,117}Sn\text{-}^{13}C)$ = 70 Hz], 96.3 [C_1], 108.4, 109.0 [2x CMe_2], 128.4 [C_m, $J(^{119,117}Sn\text{-}^{13}C)$ = 49 Hz], 128.7 [C_p, $J(^{119,117}Sn\text{-}^{13}C)$ = 11 Hz], 137.0 [C_o, $J(^{119,117}Sn\text{-}^{13}C)$ = 36 Hz], 138.9 [C_i, $J(^{119/117}Sn\text{-}^{13}C)$ = 489/467 Hz].

^{119}Sn NMR (93.3 MHz, $CDCl_3$) δ: -99.7.

Reaction of 4 with iodine.

To a solution of **4** (0.0964 g, 0.148 mmol) in $CDCl_3$ was added an equivalent of I_2 (37.8 mg). The NMR spectrum indicated the presence of three tin-sugar species, *viz.* **4** {$\delta^{119}Sn$: -99.7 ppm; $\delta^{13}C$: 6.9 [$SnCH_2$, $J(^{119/117}Sn\text{-}^{13}C)$ = 399/382 Hz,]}, 6-*O*-(3-iododiphenylstannyl)propyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**9**) {$\delta^{119}Sn$: -102.5 ppm; $\delta^{13}C$: 17.3 [$SnCH_2$, $J(^{119/117}Sn\text{-}^{13}C)$ = 475/454Hz] and 139.2 [C_i, $J(^{119/117}Sn\text{-}^{13}C)$ = 578/553 Hz,], δ^1H 5.53 [H_1, J = 5.0 Hz]} and 6-*O*-[(3-diiodophenylstannyl)propyl]-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**10**), in ratios of 1.5:4:1, based on $\delta^{119}Sn$ peak heights. More I_2 (37.8 mg) was added; the formation of 6-*O*-[(3-diiodophenylstannyl)propyl]-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, **10**, and PhI were indicated by the following NMR spectrum. Removal of all volatiles under vacuum left an oil, which decomposed on attempted crystallisation.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.29, 1.34, 1.40 and 1.56 [4 Me], 2.07-2.32 [m, 4H, H_8 + H_9], 3.41 [dd, 1H, H_6, J = 6.9 & 12.3 Hz], 3.56 [dd, 1H, $H_{6'}$, J = 3.8 & 12.3 Hz], 3.65 [dt, 1H, H_7, J = 5.3 & 9.8 Hz], 3.80-3.92 [m, 3H, H_4 + H_5 + $H_{7'}$], 4.27 [dd, 1H, H_2, J = 2.3 & 5.0Hz], 4.49 [dd, 1H, J = 2.3 & 7.8 Hz], 5.49 [d, 1H, H_1, J = 5.0 Hz], 7.09-7.74 [m, aryl, 6H].

^{13}C NMR (62.9, $CDCl_3$) δ: 24.3, 24.8, 25.8, 26.2 [4x Me], 25.5 [C_9, J($^{119/117}$Sn-^{13}C) = 510/487 Hz,], 26.8 [C_8, J(^{119,117}Sn-^{13}C) = 43 Hz], 67.1 [C_5], 69.7 [C_6], 70.1 [C_2], 70.4 [C_3], 70.8 [C_7], 71.1 [C_4], 96.1 [C_1], 108.4, 109.0 [2x CMe_2], 128.7 [C_m, J(^{119,117}Sn-^{13}C) = 79 Hz], 130.2 [C_p, J(^{119,117}Sn-^{13}C) = 17 Hz], 134.2 [C_o, J(^{119,117}Sn-^{13}C) = 61 Hz], 139.1 [C_i]. 94.3, 127.3, 130.1, 137.3 [all PhI].

^{119}Sn NMR (93.3 MHz, $CDCl_3$) δ: -228.5.

Allyl α-D-galactopyranoside, (5).

This was prepared by a published procedure.[6] The ^{13}C NMR spectrum was identical to that reported.[7]

IR (cm^{-1}) : 3351, 2963, 2934, 2882, 1453, 1406, 1134, 1120, 1109, 1088, 1070, 1059, 1022, 1008, 911, 795, 529, 469, 426.

^{1}H NMR (250 MHz, CD_3SOCD_3) δ: 3.40-3.62 [m, 13H, sugar ring protons], 3.91 [ddt, 1H, H_7, J = 1.5, 5.5, 13.6 Hz], 4.10 [ddt, 1H, $H_{7'}$, J = 1.7, 4.8 & 13.6 Hz], 4.67 [d, 1H, H_1, J = 3.1 Hz], 5.13 [ddt, 1H, H_9, J = 1.5, 1.9 & 10.4 Hz], 5.31 [ddt, 1H, $H_{9'}$, J = 1.7, 1.9 & 17.3 Hz], 5.91 [dddd, 1H, H_8, J = 4.8, 5.5, 10.4 & 17.3 Hz].

3-(Triphenylstannyl)propyl α-D-galactopyranoside, (6).

A solution of **5** (0.224 g, 1.02 mmol), Ph_3SnH (1.79 g, 5.09 mmol) and a catalytic quantity of AIBN in EtOH (5 ml) was refluxed for 9 h. The reaction mixture was cooled and filtered, then rotary evaporated. The residue was chromatographed using the chromatotron. The Ph_3SnH hydrolysis products were first removed by elution with ethyl acetate. The title compound was obtained (as an oil) by elution with ethyl acetate : methanol (9:1 v/v). Yield 31%.

Analysis found: C, 54.4; H, 5.4%. $C_{27}H_{32}O_6Sn$ requires: C,56.8; H, 5.7%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.36-1.55 [m, 2H, H_9], 1.93-2.05 [m, 2H, H_8], 2.9 [bs, 1H, OH], 3.15 [bs, 1H, OH], 3.43 [ddd, 1H, J = 6.6, 6.6 & 9.7 Hz], 3.61-4.11 [bm, 9H, $H_{7'}$ + sugar ring resonances], 4.86 [d, 1H, J = 3.6 Hz], 7.32-7.45 [m, 9H, *m*- + *p*-aryl H], 7.52-7.57 [m, 6H, *o*-aryl-H].

^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 6.6 [C_9 , J($^{119/117}$ Sn-^{13}C) = 389/371 Hz], 26.5 [C_8 , J(^{119,117}Sn-^{13}C) =18 Hz], 62.3 [C_6], 69.2 [C_5], 69.4 [C_4], 70.2 [C_2], 70.8 [C_7], 71.3 [C_3], 98.6 [C_1], 128.6 [C_m, J(^{119,117}Sn-^{13}C) = 49 Hz], 129.0 [C_p, J(^{119,117}Sn-^{13}C) = 11 Hz], 137.0 [C_o, J(^{119,117}Sn-^{13}C) = 35 Hz], 138.4 [C_i, J($^{119/117}$Sn-^{13}C) = 493/471 Hz].

^{119}Sn NMR (93.3 MHz, $CDCl_3$) δ: -100.3.

Reaction of 6 with iodine.

To a solution of **6** (26.4 mg, 43 mol) in $CDCl_3$ (0.5 ml), was added I_2 (10.9 mg, 43 mol). The NMR spectra indicated the presence of 3-(iododiphenylstannyl)propyl α-D-galactopyranoside (**11**) and PhI. Removal of all volatiles under vacuum left an oil, which decomposed on attempted crystallisation.
The resonances for 3-(iododiphenylstannyl)propyl α-D-galactopyranoside, (**11**), are :-

^{1}H NMR (250 MHz, $CDCl_3/CD_3COCD_3$) δ: 1.80-2.20 [m, 4H, H_8 + H_9], 2.90-4.20 [m, 17H, H_7 + sugar ring protons], 4.83 [d, 1H, H_1, J = 2.9 Hz], 7.06-7.75 [m, 15H, aryl-H].

^{13}C NMR (62.9 MHz, $CDCl_3/CD_3COCD_3$) δ: 14.2 [C_9], 26.9 [C_8], 62.5 [C_6], 69.7 [C_3], 70.1 [C_7], 70.3 [C_4], 70.6 [C_2], 70.9 [C_5], 99.2 [C_1], 129.0 [C_m, J($^{119\ 117}$Sn-^{13}C) = 60 Hz], 130.0 [C_p], 136.3 [C_o, J(^{119,117}Sn-^{13}C) = 47 Hz], 138.5 [C_i].

^{119}Sn NMR (93.3 MHz, $CDCl_3/CD_3COCD_3$) δ: -64.2 (broad).

1,6-Anhydro-3,4-O-isopropylidene-β-D-galactopyranose, (7).

This product was obtained from a reaction designed to produce 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, (**2**). To a solution of anhydrous $ZnCl_2$ (50.0 g), conc. H_2SO_4 (3 ml) in inadequately-dried acetone (400 ml), was added D-galactose (40.0 g, 0.22 mol). The reaction mixture was stirred at room temperature for 5 h. and an aqueous solution of sodium carbonate (80.0 g, 150 ml) was added. The precipitated zinc salts were filtered off and were washed with acetone. The acetone washings were combined with the aqueous filtrate and were rotary evaporated to remove the acetone. The aqueous solution was extracted with ether (3 x 100 ml) and the combined ethereal solutions were dried over magnesium sulphate and evaporated. The residue was fractionally distilled; during distillation, a crystalline material deposited in the condenser. This was collected and was recrystallised from ether, m.p. 153 °C, literature[8] value 151-152 °C.

Analysis found: C, 53.3; H, 6.9%. $C_9H_{14}O_5$ requires: C, 53.5; H, 7.0%.

IR (cm^{-1}) : 3482, 2992, 2943, 1387, 1260, 1213, 1161, 1134, 1057, 1028, 1016, 993, 939, 855, 806, 526.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.36 [s, 3H, Me], 1.55 [s, 3H, Me], 2.33 [bs, 1H, OH], 3.61 [ddd, 1H, H_6, J = 0.8, 5.1 & 7.6 Hz, 3.87 [s, 1H, H_2], 4.14 [d, 1H, H_6', J = 7.6 Hz], 4.22 [d, 1H, H_3, J = 7.0 Hz], 4.42-4.53 [m, 2H, H_4 + H_5], 5.39 [s, 1H, H_1].

^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 24.3 [Me], 25.7 [Me], 63.5 [C_6], 69.1 [C_4], 70.2 [C_2], 72.5 [C_5], 76.2 [C_3], 101.1 [C_6], 108.8 [*C*Me_2]

1,6-Anhydro-3,4-O-isopropylidene-2-O-[(triphenylstannyl)methyl]-β-D-galactopyranonose, (8).

To a dry DMF solution (20 ml) containing **7** (2.02g, 1.00 mmol) and excess sodium hydride (0.5 g) under a nitrogen atmosphere was added Ph_3SnCH_2I (4.91g, 1.00 mmol). The reaction mixture was stirred at RT for 6 h. On complete reaction, methanol (10 ml) was slowly added, followed by water (50 ml) and ether (50ml). The aqueous phase was separated and extracted with ether (3 x 30ml). The combined ethereal solutions were washed with water, dried over $CaCl_2$ and the solution rotary evaporated. The residue was purified using the chromatotron, eluant petrol (60-80 °C): ethyl acetate (2:1 v/v). The title compound was obtained initially, in 95% yield, as an oil, which crystallised on prolonged standing. It was recrystallised from EtOH, m.p.135 °C.

Analysis found; C, 59.2; H, 5.5%. $C_{28}H_{30}O_5Sn$ requires: C, 59.5; H, 5.4%.

IR (cm^{-1}) : 3065, 3048, 2990, 2901, 1570, 1482, 1429, 1383, 1372, 1331,1265, 1211, 1163, 1142, 1096, 1067, 1032, 997, 936, 858, 727, 698, 521, 448.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.40 [s, 3H,Me], 1.61 [s, 3H, Me], 3.51 [s, 1H, H_2], 3.64 [dd, 1H, H_6, J = 5.5 & 7.6 Hz], 4.15 [d, 1H, H_6', J = 7.6 Hz], 4.28 [d, 1H, J = 7.25 Hz], 4.44 [dd, 1H, H_4, J = 6.5 & 7.25 Hz], 4.51 [d, 1H, H_7, J = 10.2 Hz], 4.56 [dd, 1H, H_5, J = 5.5 & 6-7 Hz], 4.60 [d, 1H, H_7', J = 10.2 Hz, J($^{119/117}$Sn-^{1}H) = 21 Hz], 5.49 [s, 1H, H_1], 7.44-7.52 [m, 9H, *m*- + *p*-aryl-H], 7.67-7.73 [m, 6H, *o*-aryl-H].
^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 24.2 [Me], 25.7 [Me], 62.7 [CH_2Sn, J($^{119/117}$Sn-^{13}C) = 472/451 Hz], 62.8 [C_6], 69.3 [C_4], 71.9 [C_5], 73.3 [C_3], 82.5 [C_2], 99.3 [C_1], 108.4 [*C*Me_2], 128.5 [C_m, J(^{119,117}Sn-^{13}C) = 50

Hz, 129.1 [C_m, J($^{119\,117}$Sn-^{13}C) = 11 Hz], 137.0 [C_o, J($^{119\,117}$Sn-^{13}C) = 36 Hz], 138.0 [C_i, J($^{119/117}$Sn-^{13}C) = 509/487 Hz].

^{119}Sn NMR (93.3, $CDCl_3$) δ: -143.7.

Reaction of 8 with iodine.

To a $CDCl_3$ solution (0.5 ml) of **8** (0.113g, 0.200 mmol) was added an equivalent of iodine. The presence of one major sugar product, 1,6-anhydro-2-*O*-[(iododiphenylstannyl)methyl]-3,4-*O*-isopropylidene-β-D-galactopyranose, (**12**), and two minor tin-sugar products were indicated.

^{119}Sn NMR (93.3 MHz, $CDCl_3$) δ: -127.8 (**12**), -114.8 [Ph_3SnI], -236.2 ; peak height ratios 4.0: 1.6: 1.0.

^{1}H NMR (250 MHz, $CDCl_3$) of **12** δ: 1.38 [s, 3H, Me], 1.57 [s, 3H, Me], 3.51 [s, 1H, H_2], 3.62 [m, 1H, H_6], 4.11 [d, 1H, $H_{6'}$, J = 7.5 Hz], 4.24 [d, 1H, H_3, J = 7.4 Hz], 4.42 [m, 1H, H_4], 4.55 [d, 1H, H_7, J = 10.2 Hz], 4.60 [m, 1H, H_5], 4.64 [d, 1H, $H_{7'}$ J = 10.2 Hz], 7.4 -7.5 [m, 9H, *m*- + *p*-aryl-H], 7.6-7.8 [m, 6H, *o*-aryl-H].

Crystal Structure Determination of 8.

- Data were collected on a Delft Instruments FAST diffractometer with monochromated Mo-Kα radiation at 120 K. Corrections were made for Lorentz and polarisation effects only. The position of the tin atom was located from a Patterson vector map using[9] *SHELX-86*. The positions of the remaining non-hydrogen atoms were located on successive difference Fourier maps using[10] *SHELXL-93*. The positions of the hydrogen atoms were calculated from geometrical considerations. During the refinement, the hydrogen atoms were allowed to ride on their attached carbon atoms. Full matrix least-squares calculations with anisotropic temperature factors for the Sn, O and C atoms and common isotropic temperature factors according to type (methyl, aryl, etc) for the hydrogen atoms were calculated. The absolute configuration is based on the known stereochemistry of the carbohydrate moiety and the absolute structure parameter -0.14(4). Molecular diagrams were obtained by the program[11] *ZORTEP*. Crystal data and structure refinement details are in Table 1.

TABLE 1: CRYSTAL DATA AND STRUCTURE REFINEMENT.

Formula	$C_{28}H_{30}O_5Sn$	θ range for data collection	2.01 to 24.88°
F.W.	565.21	Index ranges	$-5 < h < 6$
Temperature	120(2) K		$-14 < k < 14$
Wavelength	0.71069 Å		$-17 < l < 20$
Crystal system	Monoclinic	Reflections collected	4664
Space Group	$P2_1$	Independent reflections	3386[R(int) = 0.0642]
Unit cell dimensions	a = 6.202(11)	Observed reflections[I>2σ(I)]	3017
(Å,°)	b = 12 .683(4)	Refinement method	Full-matrix l.s. on F^2
	c= 17.585(7)	Number of parameters	309
	α= 90	Goodness-of-fit on F^2(S)	1.061
	β = 107.34(7)	Final R indices [I > 2σ(I)]	R1 = 0.0419,wR2 = 0.1120
	γ = 90	R indices (all data)	R1 = 0.0463, wR2 = 0.1133
Volume	1320(3)Å^3	Final weighting scheme	$w = 1/[\sigma^2(Fo^2) + (0.0589P)^2]$
Density calculated	1.422 Mgm^{-3}–		where $P = (Fo^2 + 2Fc^2)/3$
Absoption coefficient	1.002 mm^{-1}	Absolute structure parameter	–0.12(4)
F(000)	576	Residual diffraction max.	1.177 eÅ^{-3}
Crystal size (mm)	0.28x0.18x0.22	Residual diffraction min.	–0.485 eÅ^{-3}

TABLE 2: SELECTED BOND LENGTHS [Å] AND ANGLES [°] FOR (8)

Sn-C(14)	2.132(11)	O(4)-C(26)	1.431(13)
Sn-C(20)	2.140(8)	O(4)-C(4)	1.445(11)
Sn-C(8)	2.140(11)	O(5)-C(1)	1.419911)
Sn-C(7)	2.146(7)	O(5)-C(6)	1.471(14)
O(1)-C(1)	1.393(12)	C(1)-C(2)	1.514(13)
O(1)-C(5)	1.447(13)	C(2)-C(3)	1.537(11)
O(2)-C(2)	1.428(9)	C(3)-C(4)	1.524(12)
O(2)-C(7)	1.440(10)	C(4)-C(5)	1.536(13)
O(3)-C(3)	1.421(10)	C(5)-C(6)	1.49(2)
O(3)-C(26)	1.439(11)	C(26)-C(27)	1.45(2)
C(26)-C(28)	1.525(13)		
C(14)-Sn-C(20)	108.2(5)	C(1)-O(1)-C(5)	101.6(8)
C(14)-Sn-C(8)	110.5(3)	C(2)-O(2)-C(7)	114.6(8)
C(20)-Sn-C(8)	110.9(5)	C(3)-O(3)-C(26)	105.6(7)
C(14)-Sn-C(7)	108.8(5)	C(26)-O(4)-C(4)	108.0(7)
C(20)-Sn-C(7)	110.0(3)	C(1)-O(5)-C(6)	104.5(8)
C(8)-Sn-C(8)	108.3(5)	O(1)-C(1)-O(5)	108.5(7)
O(2)-C(2)-C(1)	111.0(6)	O(1)-C(1)-C(2)	110.4(7)
O(2)-C(2)-C(3)	104..9(7)	O(5)-C(1)-C(2)	108.6(8)
C(1)-C(2)-C(3)	112.1(7)	O(3)-C(3)-C(4)	103.0(8)
O(3)-C(3)-C(2)	110.9(6)	C(4)-C(3)-C(2)	116.2(7)
O(4)-C(4)-C(3)	104.7(7)	O(4)-C(4)-C(5)	110.4(7)
C(3)-C(4)-C(5)	113.0(8)	O(1)-C(5)-C(6)	102.2(9)
O(1)-C(5)-C(4)	106.8(8)	C(6)-C(5)-C(4)	115.2(10)
O(5)-C(6)-C(5)	104.3(8)	O(2)-C(7)-Sn	107.1(5)
C(13)-C(8)-Sn	121.8(7)	C(9)-C(8)-Sn	119.9(8)
C(15)-C(14)-Sn	121.8(8)	C(19)-C(14)-Sn	120.3(8)
C(25)-C(20)-Sn	122.3(8)	C(21)-C(20)-Sn	119.3(8)
O(4)-C(26)-O(3)	104.4(8)	O(4)-C(26)-C(27)	110.0(9)
O(3)-C(26)-C(28)	108.1(13)	O(3)-C(26)-C(28)	108.1(9)

TABLE 3: SELECTED TORSIONAL ANGLES IN 7 and 8

	(7)	**(8)**
Pyranoid Ring		
C(1) – C(2) – C(3) – C(4)	19.9 (10)	19.6 (4)
C(2) – C(3) – C(4) – C(5)	-22.3 (11)	–20.9 (4)
C(3) – C(4) – C(5) – O(1)	50.8 (11)	49.7 (4)
C(4) – C(5) – O(1) – C(1)	-78.7 (9)	–78.5 (4)
C(5) – O(1) – C(1) – C(2)	78.9 (8)	79.3 (4)
O(1) – C(1) – C(2) – C(3)	-48.8 (9)	-49.0 (4)
1,6 - Anhydro Ring		
C(1) – O(1) – C(5) – C(6)	42.6 (10)	42.2 (4)
O(1) – C(5) – C(6) – O(5)	–30.6 (11)	–28.5 (4)
C(5) – C(6) – O(5) – C(1)	7.1 (11)	3.7 (4)
C(6) – O(5) – C(1) – O(1)	20.4 (10)	23.4 (4)
O(5) – C(1) – O(1) – C(5)	–40.1 (9)	-41.7 (4)
Dioxolane Ring		
C(3) – C(4) – O(4) – C(26)	–1 5 (9)	–3.0 (4)
C(4) – O(4) – C(26) – O(3)	23.4 (9)	21.4 (4)
O(4) – C(26) – O(3) – C(3)	–37.7 (10)	–38.4 (4)
C(26) – O(3) – C(3) – C(4)	36.0 (10)	35.6 (4)
O(3 – C(3) – C(4) – O(4)	–21.1 (8)	–19.9 (4)

RESULTS AND DISCUSSION.

The synthesis of the triphenylstannyl-galactose derivatives, obtained in this study, are shown in Scheme 1. As mentioned in the Introduction, the synthesis of a family of 6-*O*-[(1,2:3,4-di-*O*-isopropylidene)-α-D-galactopyranosyl]methyl-tin compounds, (**1**), *via* the reactions of iodomethyltin reagents with 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose, (**2**), has been reported.[1] Another nucleophilic substitution reaction of Ph_3SnCH_2I was used to prepare 1,6-anhydro-3,4-*O*-isopropylidene-2-*O*-[(triphenylstannyl)methyl]-β-D-galactopyranose, (**8**). 1,6-Anhydro-3,4-*O*-isopropylidene-β-D-galactopyranose, (**7**), was obtained in a single step from a reaction between D-galactose and undried acetone, in the presence of $ZnCl_2$ and concentrated H_2SO_4. Compound **7** has been obtained previously, less directly, from reaction of acetone with 1,6-anhydro-β-D-galactopyranose.[8] Hydrostannations of the allyl ether derivatives, **3** and **5**, were used to obtain **4** and **6**. A large excess of Ph_3SnH was employed to guarantee efficient use of the allylic sugar reagent: this resulted in the need to remove the large amounts of Ph_3SnH hydrolysis products from the reaction mixture before isolating the hydrostannylated products. Hydrostannation of the alkynyl sugar, 7,8-dideoxy-1,2;3,4-di-O-isopropylidene-D-glycero-α-D-galacto-oct-7-ynopyranose, (**13**), using Bu_3SnH has been reported [12] ; the E-adduct of **13** was formed .

Conformations in solution.

Conformations of the pyranose rings in 1,2:3,4-di-*O*-isopropylidene-a-D-galactopyranose compounds, including **1**, have been established as being twist-boat conformations.[13,14] The similarities of the ^3J(H-H) values in **4** and those of other 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose derivatives suggest the same conformation applies to the pyranose ring in **4**. The conformation of the pyranose ring in **6** could not be gained from the ^1H NMR spectrum, but it is assumed to be a chair conformation. The conformations of the pyranose rings[13] in 1,6-anhydro-β-D-galactopyranose and various non-metallated derivatives in solution have been found to be $^1C_4$. Comparison of the H-H coupling constants in the solution ^1H NMR spectra of the stannylated compound, **8**, and its precursor, **7**, indicate the configuration of the pyranose ring is unaltered on stannylation.

Crystal Structure of 8.

The atom arrangement and the numbering system for **8** are shown in Figure 1.Selected bond angles and lengths are given in Table 2. The geometry at tin is tetrahedral, with C-Sn-C bond angles varying between 108.2(5) to 110.5(3)°. The Sn-C bond lengths fall in the narrow ranges 2.132(11) to 2.146(7). The crystal structures of **7** [13] and 1,6-anhydro-β-D-galactopyranose[15] have been previously determined. As shown by the torsion angles (Table 3), **7** and **8** have very similar ring conformations in the solid state. The description of the ring conformations for **8** are (i) for the pyranose ring, a $^1C_4$ conformation, distorted towards an envelope at O1, (ii) for the 1,6-anhydro ring, a mix of an envelope (with flap at O1) and twist forms (O1 and C5 out of the plane of the other ring atoms) and (iii) for the dioxolane ring, an envelope at O3. The Cremer- Pople puckering parameters[16], obtained using the Pucker Program[17], were q_2 =0.399 and φ_2 = 349.5°, for the anhydro ring; q_2 = 0.347 and φ_2 = 1.1°, for the dioxolane ring; and Q =0.620, q_2 = 0.385, q_3 = -0.484, φ = 175.3° and θ = 141.5°, for the pyranose ring.

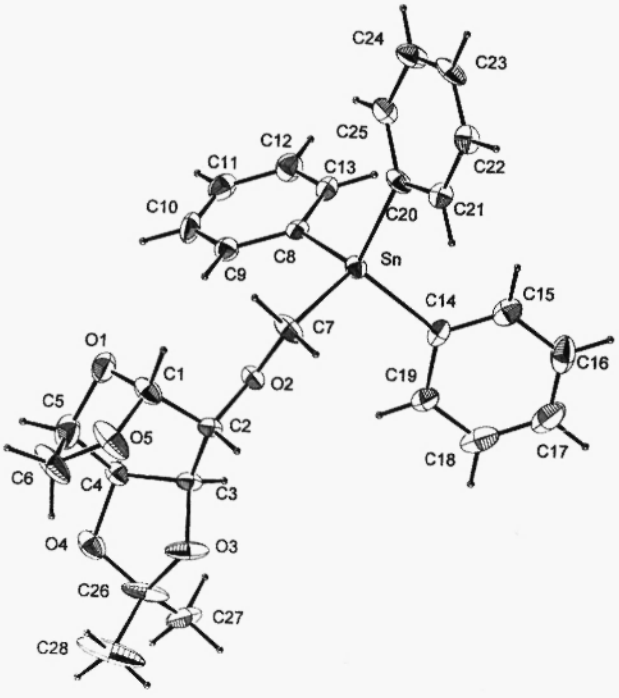


FIGURE 1: ATOM ARRANGEMENT AND NUMBERING SYSTEM FOR 8.

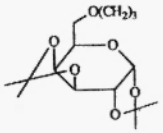
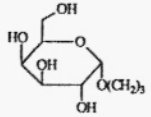
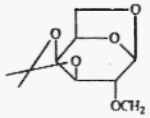
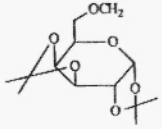
Iodo derivatives.

Organotin species, obtained from the reaction of **8** and I_2 (1:1 mol. ratio) in $CDCl_3$ at room temperature, were 1,6-anhydro-3,4-*O*-isopropylidene-2-*O*-[(iododiphenylstannyl)methyl]-β-D-galactopyranoside (**12**) , Ph_3SnI and a di-iodotin compound (**14**) (δ^{119}Sn: -236.2 ppm): the relative peak heights in the ^{119}Sn NMR spectrum were 4.0:1.6:1.0. Compound (**14**) was not unambiguously identified, but is clearly a di-iodotin species, as indicated by the comparison with the δ^{119}Sn value (-243.8 ppm) for Ph_2SnI_2 in $CDCl_3$. Of interest, the 1:1 reaction of Ph_3SnCH_2OMe (**15**) and I_2 in $CDCl_3$ also produced three tin products IPh_2SnCH_2OMe (δ^{119}Sn: -122.8 ppm), Ph_3SnI (δ^{119}Sn: -114.6 ppm) and a di-iodotin species, probably Ph_2SnI_2 (δ^{119}Sn: -243.5 ppm) in peak height ratios of 3:0.5:1.0. It is clear that in neither **8** nor **15** is there a tremendous difference in the reactivitives of the Ph-Sn and $ROCH_2$-Sn bonds. Furthermore, none of the oxygen donor groups within the sugar ligand in **8** can be providing much, if any, nucleophilic assistance during the cleavage of **8**. The solution δ^{119}Sn value for **12** (-127.5 ppm) is indicative of a four coordinate tin species, and so the sugar unit remains unchelating. The conformations of the sugar rings in **11** are similar to those in **8** and in **7**, as shown by the J(H-H) values.

Compound **6** reacted with 1 equivalent iodine to give [3-(iododiphenylstannyl)propyl] α-D-galactopyranoside (**11**); this compound exhibited a broad peak at -64.1 ppm in the ^{119}Sn NMR spectrum in $CDCl_3$/ CD_3COCD_3 solution, which is in the region expected for a 4-coordinate species of the type IPh_2SnR (R = alkyl), see Table 5.

In contrast to **11**, the mono-iodo product, 6-*O*-[3-(iododiphenyl)propyl]-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**9**), from the reaction of **6** with I_2 , is a 5-coordinate species in $CDCl_3$ solution. Thus the sugar unit in **9** is a more effective chelating ligand than that in **11.** Compound **9** also exhibits a greater reactivity than **11** towards I_2 , as shown by the ready formation of the di-iodo species, **10**.

TABLE 4: SELECTED ^{13}C AND ^{119}Sn NMR DATA FOR $I_nPh_{3-n}SnR$ (n = 0 - 2) in $CDCl_3$

R -	Ph_3SnR			IPh_2SnR			I_2PhSnR		
	$\delta^{119}Sn$	^1J (^{119}Sn - $^{13}C_i$) Hz	J (^{119}Sn - $^{13}C\alpha$) Hz	$\delta^{119}Sn$	^1J (^{119}Sn - $^{13}C_i$) Hz	J (^{119}Sn - $^{13}C\alpha$) Hz	$\delta^{119}Sn$	^1J (^{119}Sn - $^{13}C_i$) Hz	J (^{119}Sn - $^{13}C\alpha$) Hz
Me -	-92.5	510	377	-68.7	536	381	-208.8	614	403
$-(CH_2)_4SnR_2^2R^3$	-100.1[a]	483[a]	393[a]	-55.1[b]	506[b]	391[b]	-162.4[c]	549[c]	411[c]
	-99.7	489	398	-102.5	578	475	-228.5	-	506
$HO(CH_2)_3$-	-100.0	491	398	-113.1	605	493	-231.9	-	-
	-100.3	493	389	-64.1	-	-	-	-	-
	-143.7	509	472	-127.8	-	-	-	-	-
$MeOCH_2$-	-145.1	496	481	-122.8	-	508	-	-	-
	-146.2	499	484	-126.1	511	515	-	-	-

[a] $R^2 = R^3 = Ph$ [b] $R^2 = Ph$; $R^3 = I$ [c] $R^2 = I$; $R^3 = Ph$ [d] Ref 17 [e] Ref 1

ACKNOWLEDGEMENT.

The authors wish to thank the EPSRC service, based at the University of Wales, Cardiff, for the collection of the X-ray data.

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Received: January 23, 1996 - Accepted: February 1, 1996 - Accepted in revised camera-ready form: February 23, 1996