Glycosides. Part 1. New Synthesis of 1,2-*trans* *O*-Aryl Glycosides, *via* Tributyltin Phenoxides

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A new method of glycosidation of phenols has been studied. The reaction of tributyltin phenoxides **2** with 1,2,3,4,6-penta-*O*-acetyl-D-hexopyranosides **3**, **7** and **9**, in the presence of tin tetrachloride is described. Glycosides **4**, **8** and **10** have been isolated in good yields with high 1,2-*trans* selectivity. The tributyltin phenoxides **2** have been isolated in quantitative yields, starting from phenols **1** and Bu_3SnOMe. This simple method starts from the stable peracetylated sugar, an intermediate of easy access.

Glycoside synthesis has been studied extensively in the past, but it still maintains outstanding interest because of important biological implications as well as new synthetic applications, *e.g.* the preparation of chiral synthons for natural compounds. Perhaps more interesting and promising is the use of glycosides of biologically active molecules both to clarify interaction mechanisms with cell membranes and to enhance selectivity for biological targets,[1-3] mainly as anticancer and antiviral agents.[4]

A general difficulty that must be faced in the synthesis of glycosides is the stereochemical purity of the glycosyl donor and its reactivity with the substrate. Furthermore, of particular relevance is the development of a coupling reaction able to give high yields and to control the steric and electronic factors, which are responsible for the final outcome in terms of the α:β ratio.[1]

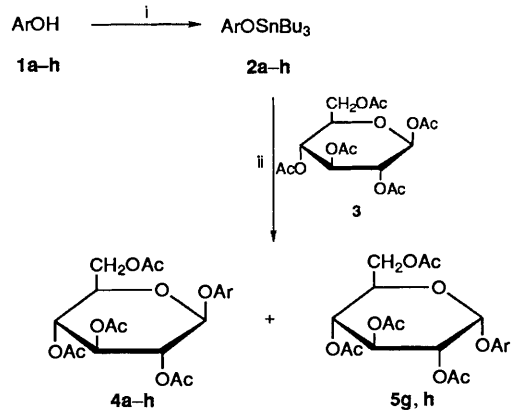
Satisfactory glycoside syntheses have been proposed and most problems have found good solutions. Main glycosidation methods for phenols are the reaction of glycosyl fluorides with phenols under various conditions,[5,6] the condensation of trimethylsilyl ethers of both the sugar and the phenol reactants,[7] and the reaction of protected sugars with phenols in the presence of 4-nitrobenzenesulfonyl chloride, silver trifluoromethanesulfonate and triethylamine.[8] Other methods have been reported as single examples, *i.e.* reaction of tetrabenzylglucopyranose with 4-methoxyphenol and dicyclohexylcarbodiimide,[9] the condensation of acetobromoglucose with tributylstannyl phenoxide and tin tetrachloride[10] and the reaction of glucose pentaacetate with 4-nitrophenol and $SnCl_4$.[11] The complexity and variety of different cases are so high that new synthetic pathways are always of utility.

We now report a practical and straightforward synthesis of glycosides of simple phenols by reaction of the readily available and stable peracetylated sugars with trialkylstannyl phenoxides, in the presence of $SnCl_4$. Yields are good and the selectivity is high.

Results

The phenols **1a–h** smoothly reacted at reflux temperature with an equimolecular amount of tributylstannyl methoxide (Bu_3SnOMe) in 1,2-dichloroethane (Scheme 1). The reaction was monitored by GLC. The stannyl phenoxides **2a–h** were formed in practically quantitative yield after 1–3 h. After simple evaporation of the reaction solvent the products were isolated in high purity. This procedure is advantageous because the stannyl phenoxides are relatively unstable compounds, which cannot be conveniently manipulated or stored.

Structure and purity of compounds **2a–h** were confirmed



Scheme 1 *Reagents and conditions:* i, Bu_3SnOMe, $ClCH_2CH_2Cl$, reflux; ii, $SnCl_4$ (30% excess), 3 Å molecular sieves, $ClCH_2CH_2Cl$, room temp.

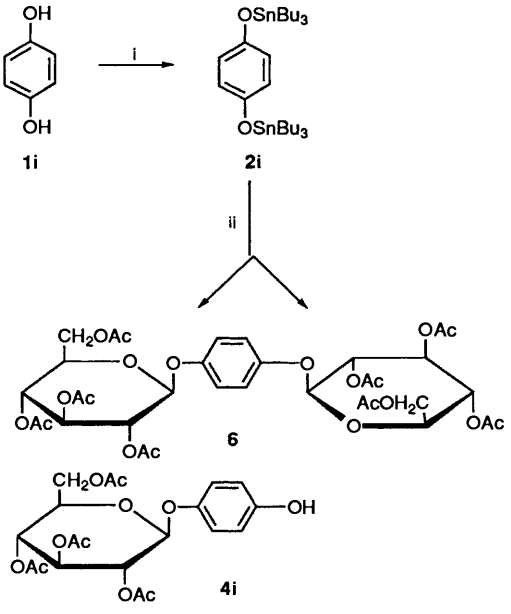
by ^1H and ^{119}Sn NMR data (δ_{Sn} 94.9–114.8 at 0.5 mol dm^{-3} concentration,[12] with values in agreement with the effects expected from the substituents on the aryl ring).[13] Compounds **2a–f** readily reacted with 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose **3** (equimolecular amounts of reactants were used) in 1,2-dichloroethane solution in the presence of a 30% excess of $SnCl_4$. The reaction was performed in the presence of 3 Å molecular sieves. Poorer yields were obtained when these auxiliaries were omitted. A 5 h reaction time at room temperature was found to be satisfactory in all cases. Column chromatography allowed purification of the β-glucosides **4a–f**. When the reaction was performed starting with 4-bromophenol **1g**, a minor amount (4%) of the α-anomer **5g** was also isolated, while with 4-nitrophenol **1h** only a trace amount of the α-anomer **5h** was formed and detected by ^1H NMR analysis (~ 1%). Hydroquinone **1i**, with an excess of Bu_3SnOMe (2 mol equiv.), formed 1,4-bis(tributylstannyloxy)benzene **2i**, which reacted with pentaacetate **3** to give both 1,4-bis(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)benzene **6** and 4-hydroxyphenyl 2,3,4,6-

tetra-*O*-acetyl-β-D-glucopyranoside **4i** (Scheme 2). Yields of isolated products are reported in Table 1. Good diastereoselectivity was also observed with different starting sugars. Under similar conditions 4-methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside **8** and 4-methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside **10** were obtained from the corresponding acetylated sugar **7** and **9**, respectively (Scheme 3 and Table 1). In both cases the configuration of the starting sugar was maintained.

Table 1 Isolated yields of *O*-aryl glycosides **4a–i**, **6**, **8** and **10**

Starting phenol **1**	Sugar derivative	1,2-*trans* Glycoside (yield, %)
a	**3**	**4a** (71)
b	**3**	**4b** (77)
c	**3**	**4c** (51)
d	**3**	**4d** (51)
e	**3**	**4e** (47)
f	**3**	**4f** (55)
g	**3**	**4g** (48)[a]
h	**3**	**4h** (23)[b]
i	**3**	**4i** (14), **6** (35)
a	**7**	**8** (70)
a	**9**	**10** (71)

[a] The α-anomer **5g** was also isolated (4%). [b] Traces of α-anomer **5h** were detected by ^{1}H NMR analysis.



Scheme 2 *Reagents and conditions:* i, Bu_3SnOMe, $ClCH_2CH_2Cl$, reflux; ii, **3**, $SnCl_4$ (30% excess), 3 Å molecular sieves, $ClCH_2CH_2Cl$, room temp.

Most of the glycosides we prepared are known and could be identified on the basis of their physical and spectroscopic properties which are in fair agreement with literature data. Compound **4e** was not described previously and was identified on the basis of its spectroscopic properties.

Discussion

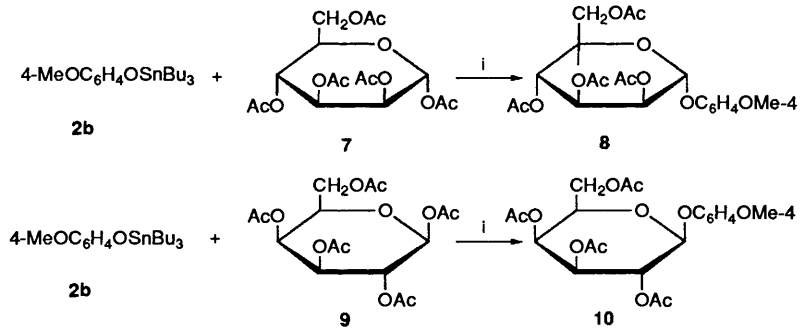
The glycosidation procedure of phenols appears to have some advantages because simple and readily available reactants are used and reaction conditions are mild. Good yields were obtained for all phenols, except 4-nitrophenol **1h**. A high 1,2-*trans* selectivity was found in all cases. It reached 100% when electron-donating groups were present on the aryl residue. The stereochemical control of the reaction appears to depend on the reaction mechanism, which is depicted in Scheme 4 for the reaction of the stannane **2** with pentaacetate **3**. Reaction of 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose **3** with $SnCl_4$ afforded complex **A** through intramolecular attack of the carbonyl oxygen of the 2-OAc group on C-1 accompanied by elimination of acetate. The resulting cationic intermediate is highly stabilized by resonance. Species **A** can be in equilibrium with the open ring isomer **B**. Intermediate **A** has already been proposed for other glycosidation reactions.[14,15] Confirmation of this mechanistic hypothesis was given by the observation that 1,2,3,4,6-penta-*O*-acetyl-α-D-glucopyranose, which lacks the stereochemistry necessary for the formation of intermediate **A**, afforded by reaction with the stannane **2b** under similar conditions a poorer yield (50%) of the β-epimer **4b** besides some by-products, probably because species **A** can be produced only after isomerization[16] of the starting peracetylated sugar to the β-epimer.

Both intermediates **A** and **B** are expected to be reactive with the stannylated phenols, but only products derived from species **A** should have good 1,2-*trans* selectivity (*anti* displacement of the leaving oxygen atom). This process is probably easier and quicker when the tin compounds are characterized by a greater nucleophilicity, which is further increased by electron-rich substituents, resulting in high yields of 1,2-*trans* products. The formation of the α-mannopyranoside **8** (*trans* configuration at C-1′ and C-2′) is in total agreement with this mechanism.

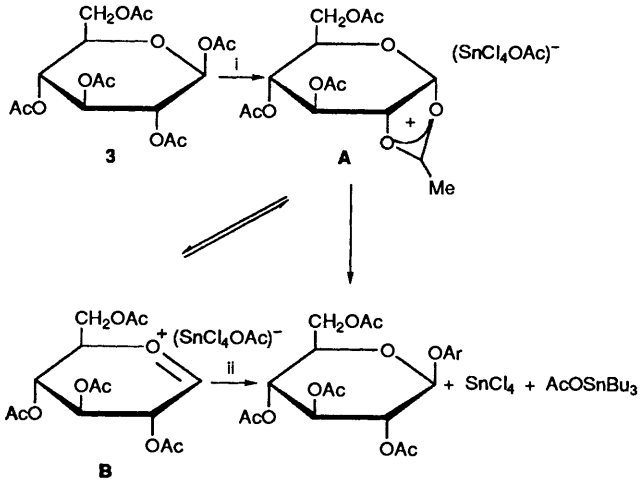
A further advantage of the present method is that it can be operated with practically equimolecular amounts of reactants,* which is not the case with most known procedures, resulting in an easier purification of the end products.

Only in the case of phenols **1g** and **1h** was a minor amount of α-anomer obtained. A possible explanation may be found in the alternative reaction mechanism entailing intermediate **B**, which is expected to have minor steric control. It is worth noting that

* Experiments demonstrated that use of an excess of sugar and $SnCl_4$ did not affect the final yield to any important extent.



Scheme 3 *Reagents and conditions:* i, $SnCl_4$ (30% excess), 3 Å molecular sieves, $ClCH_2CH_2Cl$, room temp.



Scheme 4 *Reagents:* i, $SnCl_4$; ii, $ArOSnBu_3$

the β-epimer **4d** does not equilibrate with its α-isomer under the same reaction condition.*

Experimental

M.p.s were determined using a Büchi 510 (capillary) apparatus. Optical rotations were measured with a Perkin-Elmer 241 polarimeter; $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. NMR spectra were obtained with either a Bruker AC 200 or an EM-390 Varian instrument. Chemical shifts (δ) are given in ppm and coupling constants (J) are given in Hz. Column chromatography was performed on silica gel [Kieselgel 60–70 230 ASTM (Merck)]. GLC analyses were performed with OV 101 (0.5 m, o.d. $\frac{1}{8}''$, material SS, mesh 100/120, support Chrom-WHP) column.

Materials.—Bu_3SnOMe, $SnCl_4$, starting phenols **1** and sugars **3** and **9** are commercially available. 1,2,3,4,6-Penta-*O*-acetyl-α-D-mannopyranoside **7** was prepared according to a literature procedure.[17] 1,2-Dichloroethane was dried over 4 Å molecular sieves.

General Procedure for the Preparation of Tributyltin Phenoxides **2a–i**.—Under nitrogen, Bu_3SnOMe (0.95 cm^3, 3.3 mmol) was added dropwise to a solution of a phenol **1a–h** (3 mmol) in 1,2-dichloroethane (10 cm^3) at reflux. In the case of hydroquinone **1i** an excess of Bu_3SnOMe (1.9 cm^3, 6.6 mmol) was used. The mixture was stirred for 2 or 3 h, until the starting materials were no longer detectable (GLC analysis). The solvent was evaporated off under reduced pressure. The products obtained were pure compounds (^1H and ^{119}Sn NMR analyses), and could be used for further reaction.

Tributyltin phenoxide **2a**. Oil; $\delta_{Sn}(CDCl_3$; 0.5 mol $dm^{-3})$ 105.2; $\delta_H(CDCl_3)$ 0.94 (9 H, t, J 7.5), 1.27–1.59 (12 H, m), 1.63–1.72 (6 H, m), 6.72–6.83 (3 H, m, ArH) and 7.15–7.23 (2 H, m, ArH).

Tributyltin 4-methoxyphenoxide **2b**. Oil; $\delta_{Sn}(CDCl_3$; 0.5 mol $dm^{-3})$ 101.9; $\delta_H(CDCl_3)$ 0.93 (9 H, t, J 7.2), 1.18–1.41 (12 H, m), 1.54–1.65 (6 H, m), 3.70 (3 H, s, 4-OMe) and 6.60 and 6.70 (4 H, A_2B_2, J 9, ArH).

Tributyltin 2-methoxyphenoxide **2c**. Oil; $\delta_{Sn}(CDCl_3$; 0.5 mol $dm^{-3})$ 94.9; $\delta_H(CDCl_3)$ 0.89 (9 H, t, J 7), 1.14–1.41 (12 H, m), 1.52–1.68 (6 H, m), 3.80 (3 H, s, 2-OMe) and 6.71–6.81 (4 H, m, ArH).

Tributyltin 4-chlorophenoxide **2d**. Oil; $\delta_{Sn}(CDCl_3$; 0.5 mol $dm^{-3})$ 108.4; $\delta_H(CDCl_3)$ 0.92 (9 H, t, J 7), 1.16–1.41 (12 H, m), 1.50–1.63 (6 H, m) and 6.90 and 7.38 (4 H, A_2B_2, J 9, ArH).

Tributyltin 3,4-(methylenedioxy)phenoxide **2e**. Oil; $\delta_{Sn}(CDCl_3$; 0.5 mol $dm^{-3})$ 104.2; $\delta_H(CDCl_3)$ 0.90 (9 H, t, J 7), 1.18–1.42 (12 H, m), 1.52–1.68 (6 H, m), 5.86 (2 H, s, CH_2) and 6.10, 6.28 and 6.59 (3 H, ABX, J_{AX} 2.6, J_{AB} 8.4, 2-, 5- and 6-H).

Tributyltin 2-naphthoxide **2f**. Oil; $\delta_{Sn}(CDCl_3$; 0.5 mol $dm^{-3})$ 105.9; $\delta_H(CDCl_3)$ 0.92 (9 H, t, J 7), 1.28–1.47 (12 H, m), 1.60–1.72 (6 H, m) and 7.00–7.75 (7 H, m, ArH).

Tributyltin 4-bromophenoxide **2g**. Oil; $\delta_{Sn}(CDCl_3$; 0.5 mol $dm^{-3})$ 108.3; $\delta_H(CDCl_3)$ 0.90 (9 H, t, J 7), 1.13–1.42 (12 H, m), 1.50–1.67 (6 H, m) and 6.97 and 7.41 (4 H, A_2B_2, J 9, ArH).

Tributyltin 4-nitrophenoxide **2h**. Oil; $\delta_{Sn}(CDCl_3$; 0.5 mol $dm^{-3})$ 114.8; $\delta_H(CDCl_3)$ 0.91 (9 H, t, J 7), 1.30–1.40 (12 H, m), 1.59–1.69 (6 H, m) and 6.63 and 7.08 (4 H, A_2B_2, J 9, ArH).

1,4-Bis(tributylstannyloxy)benzene **2i**. Oil; $\delta_{Sn}(CDCl_3$; 0.5 mol $dm^{-3})$ 97.2; $\delta_H(CDCl_3)$ 0.82 (9 H, t, J 7.2), 1.01–1.35 (12 H, m), 1.58–1.61 (6 H, m) and 6.44 (4 H, s, ArH).

General Procedure for the Preparation of Aryl Glycosides **4a–i**.—Under nitrogen, $SnCl_4$ (0.46 cm^3, 3.9 mmol) was added to a solution of a sugar **3**, **7** or **9** (3 mmol) in 1,2-dichloroethane (10 cm^3) containing 3 Å molecular sieves. The solution was stirred for 15 min, then the corresponding tributyltin phenoxide **2a–h** (3 mmol) was added. In the case of compound **2i** the sugar **3** (6 mmol, 2 mol equiv.) and $SnCl_4$ (0.91 cm^3, 7.8 mmol) were used. After the mixture had been stirred for 5 h, saturated aq. $NaHCO_3$ was added. The insoluble materials were filtered off and washed twice with 1,2-dichloroethane. Organic materials were extracted with 1,2-dichloroethane, and the combined organic phases were washed with 10% aq. NaF, dried (Na_2SO_4), and concentrated. The residue was chromatographed on a silica gel column with AcOEt–C_6H_{14} (1:1.5 v/v) to give the pure glycosides.

Phenyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside **4a**. 71%; m.p. 120–122 °C (lit.,[5] 125 °C); $[\alpha]_D^{25}$ −18.3 (*c* 1, $CHCl_3$) {lit.,[5] $[\alpha]_D^{23}$ −21.0 (*c* 1, $CHCl_3$)}.

4-Methoxyphenyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside **4b**. 77%; m.p. 97.4–98.3 °C (lit.,[5] 98.5 °C); $[\alpha]_D^{25}$ −15.3 (*c* 1, $CHCl_3$) {lit.,[5] $[\alpha]_D^{23}$ −15.5 (*c* 1, $CHCl_3$)}.

2-Methoxyphenyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside **4c**. 51%; m.p. 153–153.4 °C (lit.,[18] 155–156 °C); $[\alpha]_D^{25}$ −28.8 (*c* 1, $CHCl_3$) {lit.,[18] $[\alpha]_D^{21}$ −29 (*c* 1, $CHCl_3$)}.

4-Chlorophenyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside **4d**. 51%; m.p. 123–124 °C (lit.,[5] 124 °C); $[\alpha]_D^{25}$ −19.9 (*c* 1, $CHCl_3$) {lit.,[5] $[\alpha]_D^{23}$ −19.3 (*c* 1, $CHCl_3$)}.

3,4-(Methylenedioxy)phenyl 2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside **4e**. 47%; m.p. 149.8–151.1 °C (Found: C, 53.8; H, 5.1. $C_{21}H_{24}O_{12}$ requires C, 53.63; H, 5.16%); $[\alpha]_D^{25}$ −0.9, $[\alpha]_{365}^{25}$ −16.6 (*c* 1, $CHCl_3$); $\delta_H(CDCl_3)$ 2.03 (3 H, s, AcO), 2.03 (3 H, s, AcO), 2.07 (3 H, s, AcO), 2.09 (3 H, s, AcO), 3.76–3.84, 4.16 and 4.29 (3 H, ABX, J_{AX} 2.5, J_{BX} 5.4, J_{AB} 12, 5'-H and 6'-H_2), 4.92 (1 H, d, $J_{1',2'}$ 7.5, 1'-H), 5.09–5.28 (3 H, m, 2'-, 3'- and 4'-H), 5.94 (2 H, s, CH_2) and 6.45, 6.59 and 6.69 (3 H, ABX, J_{AX} 2.6, J_{AB} 8.4, 2-, 5- and 6-H); $\delta_C(CDCl_3)$ 20.7, 62.0, 68.4, 69.9, 71.2, 72.0, 72.8, 100.7, 101.6, 108.1, 109.8, 143.8, 148.2, 152.1, 169.4, 169.5, 170.3 and 170.7.

2-Naphthyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside **4f**. 55%; m.p. 124.5–125.5 °C (lit.,[18] 135–136 °C); $[\alpha]_D^{25}$ −17.8 (*c* 1, $CHCl_3$) {lit.,[18] $[\alpha]_D^{21}$ −19 (*c* 1, $CHCl_3$)}.

4-Bromophenyl 2,3,4,6-tetra-O-acetyl-D-glucopyranoside **4g** *and* **5g**. The α and β anomers were obtained as solids in 48 and 4% yield, respectively. β-Anomer **4g**: m.p. 129.8–130 °C (lit.,[5] 132 °C); $[\alpha]_D^{25}$ −17.1 (*c* 1, $CHCl_3$) {lit.,[5] $[\alpha]_D^{23}$ −17.2 (*c* 1, $CHCl_3$)}. α-Anomer **5g**: m.p. 111–112 °C (lit.,[5] 112.5 °C);

* An attempt at isomerization was performed by addition of $SnCl_4$ (3.9 mmol) to a solution of the phenol **4g** (3 mmol) in 1,2-dichloroethane at room temperature. After 5 h, no α-anomer was detectable by TLC analysis.

$[\alpha]_D^{25}$ +155.17 (*c* 1, $CHCl_3$) {lit.,[5] $[\alpha]_D^{23}$ +152 (*c* 1, $CHCl_3$)}.

4-*Nitrophenyl* 2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranoside* **4h**. 23%; m.p. 173–174.3 °C (lit.,[5] 174–174.5 °C); $[\alpha]_D^{25}$ −38.25 (*c* 1, $CHCl_3$) {lit.,[5] $[\alpha]_D^{23}$ −34 (*c* 1, $CHCl_3$)}.

4-*Hydroxyphenyl* 2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranoside* **4i**. 14%; m.p. 135–136 °C (lit.,[19] 136 °C); $[\alpha]_D^{25}$ −35 (*c* 1, $CHCl_3$) {lit.,[19] $[\alpha]_D^{23}$ −36 (*c* 1, $CHCl_3$)}.

1,4-*Bis*(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyloxy*)*benzene* **6**. 35%; m.p. 188–189.3 °C (lit.,[5] 195–196 °C); $[\alpha]_D^{25}$ −15.7 (*c* 1, $CHCl_3$) {lit.,[5] $[\alpha]_D^{23}$ −16 (*c* 1, $CHCl_3$)}.

4-*Methoxyphenyl* 2,3,4,6-*tetra*-O-*acetyl*-α-D-*mannopyranoside* **8**. 70%; m.p. 100–102 °C (lit.,[20] 101–102 °C); $[\alpha]_D^{25}$ +75 (*c* 1, $CHCl_3$) {lit.,[21] $[\alpha]_D^{23}$ +70 (*c* 1, $CHCl_3$)}.

4-*Methoxyphenyl* 2,3,4,6-*tetra*-O-*acetyl*-β-D-*galactopyranoside* **10**. 71%; m.p. 101–102 °C (lit.,[22] 102–103 °C); $[\alpha]_D^{25}$ +3.1 (*c* 1, $CHCl_3$) {lit.,[22] $[\alpha]_D^{25}$ +2.9 (*c* 1, $CHCl_3$)}.

Acknowledgements

This work was supported by INDENA S.p.A. (Milan).

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Paper 3/06883H
Received 17*th November* 1993
Accepted 29*th November* 1993