Carbohydrate Research, 90 (1981) 61–69
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

SYNTHESIS OF 1D-2-*O*- AND 1D-5-*O*-(α-D-GALACTOPYRANOSYL)-4-*O*-METHYL-*chiro*-INOSITOL: PREFERENCE FOR EQUATORIAL HYDROXYL GROUPS IN THE IMIDATE GALACTOSYLATION PROCEDURE

PER J. GAREGG

Department of Organic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm (Sweden)

AND INGEMAR KVARNSTRÖM

Department of Chemistry, University of Linköping, S-581 83 Linköping (Sweden)

(Received July 21st, 1980; accepted for publication, August 11th, 1980)

ABSTRACT

1D-2-*O*-(α-D-Galactopyrano::yl)-4-*O*-methyl-*chiro*-inositol, identical to a galactosylpinitol previously isolated from seeds of *Trifolium subterraneum*, has been synthesised, together with an isomer, 1D-5-*O*-(α-D-galactopyranosyl)-4-*O*-methyl-*chiro*-inositol. In both syntheses, the imidate method of galactosylation was used on inositol derivatives having one axial and one equatorial hydroxyl-group free. Good selectivity of the reagent for the equatorial hydroxyl groups was demonstrated.

INTRODUCTION

Galactosylpinitols have been identified[1] from extracts of such leguminous seeds as *Glycine max*, *Cicer arietinum* L., *Lens esculenta*, and *Phaseolus vulgaris* L. One of these compounds has tentatively been identified, mainly on the basis of the mass spectrum of the per-trimethylsilylated derivative, as 1D-1-*O*-(α-D-galactopyranosyl)-4-*O*-methyl-*chiro*-inositol. A galactosylpinitol isolated from extracts of seeds of subterranean clover (*Trifolium subterraneum*) has been assigned the structure 1D-2-*O*-(α-D-galactopyranosyl)-4-*O*-methyl-*chiro*-inositol, based on Smith-degradation studies and other evidence[2].

We now report on a straightforward synthesis of 1D-2-*O*-(α-D-galactopyranosyl)-4-*O*-methyl-*chiro*-inositol (**9**) and also of a positional isomer (**11**) having the α-D-galactopyranosyl group linked to O-5 of 1D-4-*O*-methyl-*chiro*-inositol. Compound **9** is identical with the galactosylpinitol from *T. subterraneum*[2].

RESULTS AND DISCUSSION

Pinitol was converted into the 1,2:5,6-diorthobenzoate **1** by treatment with triethyl orthobenzoate in *N*,*N*-dimethylformamide, using toluene-*p*-sulfonic acid as the catalyst. Crude **1** was benzylated, yielding 3-*O*-benzylpinitol 1,2:5,6-di(ethyl

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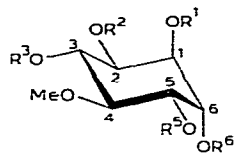
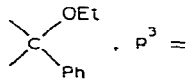
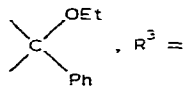


Pinitol · $R^1 = R^2 = R^3 = R^5 = R^6 = H$

1 $R^1 = R^2$ and $R^5 = R^6 =$  , $R^3 = H$

2 $R^1 = R^2$ and $R^5 = R^6 =$  , $R^3 = Bzl$

3 $R^1 = R^5 = Bz$, $R^2 = R^5 = H$, $R^3 = Bzl$

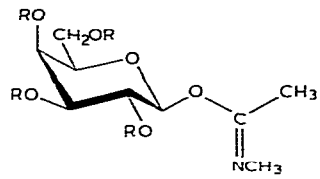
4 $R^1 = R^6 = H$, $R^2 = R^5 = Bz$, $R^3 = Bzl$

5 $R^1 = R^5 = Bz$, $R^2 = R^6 = H$, $R^3 = Bzl$

5a $R^1 = R^5 = Bz$, $R^2 = R^6 = Ac$, $R^3 = Bzl$

6 $R^1 = R^5 = H$, $R^2 = R^6 = Bz$, $R^3 = Bzl$

6a $R^1 = R^5 = Ac$, $R^2 = R^6 = Bz$, $R^3 = Bzl$



7 R = Bzl

orthobenzoate) (**2**). Acid-catalysed ring-opening of ortho esters in pyranoid systems gives axial esters as the main products[3]. However, the corresponding treatment of **2** afforded a mixture of the four possible dibenzoates, in which the equatorial/axial and axial/equatorial isomers **5** and **6** preponderated. Explanations for the mainly axial orientation of the acyl substituent in the ring opening of 1,2-(ortho esters) in six-membered ring systems include arguments for the preferential cleavage of the pseudo-equatorial oxygen–acyl carbon bond in preference to the pseudo-axial ones[3,4]. For 1,2-(ortho esters) in cyclohexanes, the angle between the two O-1 and O-2 bonds is ~30°. However, this angle in **2** is smaller, because of flattening of the ring around the C-5, C-6, C-1, C-2 part of the molecule and thus there is less of a difference between pseudo-axial and pseudo-equatorial bonds, which might explain the results obtained.

N.m.r. spectra, particularly relevant for the assignment of the various structures, are given in Tables I–III. Partial assignments of signals for compounds **3–6a** are given in Table I. The results show that all of the compounds are dibenzoates. Hydrogens on benzoyloxylated carbons appear downfield in the spectra. The small coupling constants of the presumed H-1 and H-6 signals in the spectrum of **3** indicate that the benzoyl groups are diaxially situated and therefore at O-1 and O-6. Similarly, the coupling constants (*a/a* and *a/e*) of the presumed H-2 and H-5 signals in the spectrum of **4** indicate that the benzoyl groups are at O-2 and O-5. The ^{1}H-n.m.r. spectral data obtained for compounds **5–6a** similarly show that these are the 1,5- and 2,6-dibenzoates, but do not distinguish between **5** and **6**, each having an axial and an equatorial benzoate group, with similar geometry at adjacent carbon atoms.

Using as a basis the reported resonance frequencies for the ^{13}C-n.m.r. spectra

TABLE I

^{1}H-N.M.R. DATA ($CDCl_3$) FOR COMPOUNDS 3–6a[a]

Compound	*H-1*	*H-2*	*H-3* *H-4*	*H-5*	*H-6*	*OH*	*OAc*	*OMe*	*PhCH$_2$*	*Aromatic H*
3	5.66–5.69 (m, 2 H)	4.1–4.4 (m, 2 H)	← 3.87 → (t, *J* 7.8 Hz) or ← 3.64 → (t, *J* 7.8 Hz)	4.1–4.4 (m, 2 H)	5.66–5.69 (m, 2 H)	2.81 (d, *J* 5.1 Hz) 2.93 (d, *J* 5.4 Hz)		3.68 (s)	4.85 (s)	7.2–7.6 (11 H) 7.9–8.0 (4 H)
4	4.34 (bs, 2 H)	5.55 (dd, 2 H, $J_{1,2}$ 4.9 and $J_{2,3}$ 9.0 Hz)	← 3.92 → (t, *J* 8.9 Hz) or ← 4.15 → (t, *J* 8.9 Hz)	5.55 (dd, 2 H, $J_{5,6}$ 4.9 and $J_{4,5}$ 9.0 Hz)	4.34 (bs, 2 H)	3.09 (bs, 2 H)		3.53 (s)	4.72 (d, *J* 11 Hz) 4.79 (d, *J* 11 Hz)	7.1–7.5 (11 H) 7.9–8.1 (4 H)
5	5.56 (dd, *J* 3.2 and 4.6 Hz)	4.18–4.38 (m, 2 H)	3.82–3.91 (m, 2 H)	5.43 (dd, $J_{5,6}$ 3.4 and $J_{4,5}$ 9.0 Hz)	4.18–4.38 (m, 2 H)	2.62 (d, *J* 3.9 Hz) 2.99 (d, *J* 4.1 Hz)		3.59 (s)	4.80 (d, *J* 11 Hz) 4.91 (d, *J* 11 Hz)	7.1–7.6 (11 H) 7.9–8.1 (4 H)
5a	← 5.33–5.65 → (m, 4 H)		← 3.75–4.09 → (m, 2 H)	← 5.33–5.65 → (m, 4 H)			1.96 (s), 2.15 (s)	3.61 (s)	4.75 (d, *J* 11 Hz) 4.84 (d, *J* 11 Hz)	7.2–7.6 (11 H) 7.9–8.1 (4 H)
6	4.25–4.45 (m, 2 H)	5.49 (dd, $J_{1,2}$ 3.3 and $J_{2,3}$ 9.6 Hz)	← 3.63 → (t, *J* 8.9 Hz) or ← 4.11 → (t, *J* 9.1 Hz)	4.25–4.45 (m, 2 H)	5.60 (t, *J* 3.7 Hz)	2.94 (bs) 3.29 (bs)		3.67 (s)	4.76 (d, *J* 11 Hz) 4.79 (d, *J* 11 Hz)	7.2–7.6 (11 H) 7.9–8.1 (4 H)
6a	← 5.28–5.74 → (m, 4 H)		← 3.78 → (t, *J* 9.1 Hz) or ← 4.07 → (t, *J* 9.3 Hz)	← 5.28–5.74 → (m, 4 H)			2.04 (s), 2.14 (s)	3.62 (s)	4.79 (d, *J* 11 Hz) 4.85 (d, *J* 11 Hz)	7.2–7.6 (11 H) 7.9–8.1 (4 H)

[a]For ring protons, each signal is 1 H, unless otherwise stated.

TABLE II

^{13}C-N.M.R. DATA FOR COMPOUNDS 3–6 (EXCLUDING AROMATIC CARBONS)

Compound	*Assignment of Bz*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*CH_3O*	*C=O*
Pinitol[a]	—	72.3	71.4	73.0	83.6	70.7	72.5	60.7	—
3	1,6	74.9 or 75.6	70.1 or 70.2	80.4	82.7	70.1 or 70.2	74.9 or 75.6	60.8	165.1
4	2,5	69.8	73.8 or 74.1	78.8	81.1	73.8 or 74.1	69.8	60.9	165.6
5	1,5	74.1	67.6 or 69.3	81.0	81.0	72.9	67.6 or 69.3	60.9	165.4 165.7
6	2,6	69.4	73.2 or 74.0	79.1	83.7	67.6	73.2 or 74.0	61.3	165.4 165.9

[a]These measured values correspond closely to those published[5].

of pinitol[5], partial assignments of the various signals in the corresponding spectra for the pinitol intermediates **3**–**6a** may be made (Table II).

These data confirm the above structural assignments and give further information. The 1,6-dibenzoate **3** shows a single carbonyl signal at 165.1 p.p.m., and the 2,5-dibenzoate **4** a corresponding, single signal at 165.6 p.p.m. On the other hand, the two dibenzoates **5** and **6** having one axial and one equatorial benzoate group show two carbonyl signals. This corroborates the conclusion, drawn from the ^{1}H-n.m.r. study, that **3** and **4** are the diaxial 1,6- and diequatorial 2,5-dibenzoates, but still does not show which is which of **5** and **6**. Upon substitution with a benzoate group, the substituted carbon atoms in **3**–**6a** show the expected downfield shift of the signal given by the carbon atom in the benzoylated position. The expected, corresponding upfield-shifts of the signals for neighbouring carbon atoms are also generally observed. The chemical shift given by C-4 is particularly useful in assigning the structures. In **4** as well as in **5**, upfield shifts of 2.5 and 2.6 p.p.m. are observed relative to that for the C-4 signal of pinitol, indicating benzoyl substitution at the adjacent C-5. This further distinguishes **3** from **4** and, more importantly, it clearly distinguishes **5** from **6**. Moreover, upon acetylation of the 1,5-dibenzoate **5** to give **5a**, the C-4 signal is only shifted from 81.0 to 81.2 p.p.m., whereas upon acetylation of the 2,6-dibenzoate **6** to give **6a**, the C-4 signal is shifted from 83.7 to 81.1 p.p.m., due to substitution by acetyl at the adjacent C-5 in **6a**, but not in **5a**.

The 1,5-dibenzoate **5** is a possible precursor of the galactosylpinitol **9**. Instead of following a route to an intermediate having only HO-2 unsubstituted, advantage was taken of the expected difference in reactivity of the axial HO-6 and equatorial HO-2 in **5**. Galactosylation of **5** with 1.9 mol. equiv. of the imidate[6] **7** in benzene at

TABLE III

^{13}C-N.M.R. DATA FOR **9**, **11**, AND THE NATURAL PRODUCT

Compound	*Pinitol carbon atoms*							*Galactopyranosyl carbon atoms*					
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	CH_3O	*C-1′*	*C-2′*	*C-3′*	*C-4′*	*C-5′*	*C-6′*
Pinitol	72.3	71.4	73.0	83.6	70.7	72.5	60.7	—	—	—	—	—	—
Methyl α-D-galactopyranoside[a]	—	—	—	—	—	—	—	100.2	69.1	70.4	70.1	71.6	62.2
9	68.3	76.4	71.6	83.6	70.0	71.9	60.7	96.4	69.1	70.6	70.1	71.6	61.7
	(Δ −4.0)	(Δ +5.0)	(Δ −1.4)	(Δ 0)	(Δ −0.7)	(Δ −0.6)	(Δ 0)						
11	71.7	71.3	73.2	82.2	75.1	68.0	61.4	95.8	69.0	70.4	69.9	71.7	61.7
	(Δ −0.6)	(Δ −0.1)	(Δ +0.2)	(Δ −1.4)	(Δ +4.4)	(Δ −4.5)	(Δ +0.7)						
Galactosylpinitol	68.3	76.4	71.6	83.6	70.0	71.9	60.7	96.4	69.1	70.6	70.1	71.6	61.8

[a]These measured values correspond closely to those published[7].

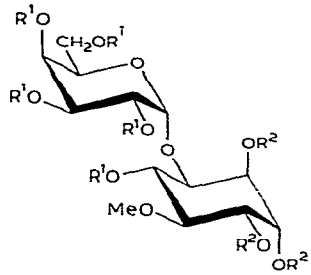
room temperature for 48 h, using toluene-*p*-sulfonic acid as catalyst, followed by debenzoylation and chromatographic purification, gave the monogalactosyl derivative **8** in 43% yield. The corresponding, partial galactosylation of **6**, using the imidate **7**, followed by debenzoylation and chromatographic purification, yielded the monogalactosyl derivative **10** in 40% yield. T.l.c. of the reaction mixtures from the syntheses of **8** and **10** revealed only minor amounts of other products of galactosylation. The attachment of the galactopyranosyl group in **8** and **10** to equatorial positions was demonstrated by ^{1}H-n.m.r. spectroscopy of the derived, debenzoylated and acetylated **8a** and **10a**. For both compounds, this showed coupling constants corresponding to two axial and one equatorial acetoxyl groups in the pinitol residue. This finding indicates a considerable difference in reactivity between the axial and equatorial hydroxyl groups in **5**, as well as in **6**, on galactosylation by the imidate procedure. Catalytic hydrogenolysis of **8** and **10** afforded **9** and **11**, respectively.

Comparisons of the ^{13}C-n.m.r. spectra of **9** and **11** with those reported for pinitol[5] and for methyl α-D-galactopyranoside[7], respectively, show (Table III) the expected downfield shifts for the C-2 signal in the pinitol residue for **9** and the corresponding upfield-shifts for the signals given by neighbouring C-1 and C-3. Apart from the expected difference in the chemical shift for the C-1′ signal, the remaining signals given by carbon atoms in the galactosyl group are close to those for methyl α-D-galactopyranoside. The ^{13}C-n.m.r. spectrum of the galactosylpinitol from *T. subterraneum*[2] was superposable on that given by **9**. In the ^{13}C-n.m.r. spectrum of **11**, the expected downfield-shift is observed for the C-5 signal from the pinitol residue. Furthermore, an upfield shift of 0.7 p.p.m. in the methoxyl resonance for **11**, as compared to that for pinitol and not observed for **9**, is indicative of substitution at C-5 in the pinitol residue of **11**, but not in **9**. The frequencies observed for the C-2′, C-3′, C-4′, C-5′, and C-6′ signals in the α-D-galactosyl group in **11** are close to the corresponding signals for methyl α-D-galactopyranoside[7]. The expected upfield-shifts for the C-4 and C-6 resonance in **11**, as compared to the corresponding signals for pinitol, are observed in the spectrum given by **11**. The α-D configuration at C-1′ in the galactopyranosyl residue of **9** and **11** is shown by the high optical rotation as well as by the n.m.r. data.

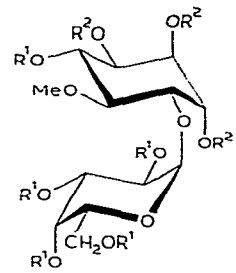
These considerations of spectral data for intermediates, final products, and mode of synthesis, and the identical properties of **9** and the galactopyranosylpinitol from *T. subterraneum*[2] shown in Table IV, taken together with the identical ^{1}H- and ^{13}C-n.m.r. spectra obtained for the two compounds, confirm that the natural product has the structure **9**.

EXPERIMENTAL

General methods. — Melting points are corrected. Concentrations were performed on a rotary evaporator at <40° (bath). Optical rotations were measured at 20° with a Perkin–Elmer 241 instrument; ^{1}H- and ^{13}C-n.m.r. spectra were recorded at 99.6 and 25.05 MHz, respectively, with a Jeol JNM FX 100 instrument. Chemical



8 R^1 = Bzl, R^2 = H
8a R^1 = Bzl, R^2 = Ac
9 R^1 = R^2 = H (natural product)



10 R^1 = Bzl, R^2 = H
10a R^1 = Bzl, R^2 = Ac
11 R^1 = R^2 = H

shifts are reported as p.p.m. downfield from internal and external tetramethylsilane for solutions in $CDCl_3$ and D_2O respectively. T.l.c. was performed on precoated, silica gel plates (F_{254} Merck) with detection by u.v. light or by charring with sulfuric acid. Column separations were performed on silica gel 60 (0.040–0.063 mm, Merck).

The purity of each new compound was carefully ascertained by t.l.c. with a solvent system which gave R_F values of ~0.5. Identity was ascertained by n.m.r. spectra, which invariably were in accordance with those expected. Anomeric identity and purity were ascertained by careful observation of anomeric signals in the ^1H- and ^{13}C-n.m.r. spectra. Selected n.m.r. parameters for compounds other than those in the Tables are given below.

Acid-catalysed opening of the cyclic orthoester groups in 1D-*3*-O-*benzyl-4*-O-*methyl*-chiro-*inositol 1,2*:*5,6-di*(*ethyl orthobenzoate*) (**2**). — A solution of 1D-4-*O*-methyl-*chiro*-inositol (pinitol) (0.50 g, 2.58 mmol), triethyl orthobenzoate (7.0 ml, 30.2 mmol), and toluene-*p*-sulfonic acid (40 mg) in *N*,*N*-dimethylformamide (8 ml) was kept at room temperature for 8 h, and then diluted with dichloromethane. The solution was extracted with aqueous sodium hydrogencarbonate and water, dried (Na_2SO_4), filtered, and concentrated, to give crude 1D-4-*O*-methyl-*chiro*-inositol 1,2:5,6-di(ethyl orthobenzoate) (**1**, 1.3 g).

A mixture of crude **1** (1.3 g, ~2.6 mmol), benzyl bromide (6 ml, 52 mmol), and powdered potassium hydroxide (2.0 g) was stirred for 2 h at 130–140° and then cooled. Water was added and the mixture was extracted with chloroform. The extract was washed with water, dried (Na_2SO_4), filtered, and concentrated, to give crude **2** (1.5 g).

Crude **2** (1.5 g) was treated with 80% aqueous acetic acid (50 ml) at room temperature for 10 min. The solution was concentrated to dryness. The resulting mixture was fractionated by column chromatography (toluene–ethyl acetate, 4:1). Four main components were obtained. Eluted first was 1D-*1,6-di*-O-*benzoyl-3*-O-*benzyl-4*-O-*methyl*-chiro-*inositol* (**3**; 90 mg, 7%), m.p. 150–151° (from ether–light petroleum), $[\alpha]_D$ −2° (*c* 1, chloroform).

Eluted second was 1D-*2,5-di*-O-*benzoyl-3*-O-*benzyl-4*-O-*methyl*-chiro-*inositol* (**4**; 70 mg, 6%), $[\alpha]_D$ +90° (*c* 0.9, chloroform).

TABLE IV

COMPARISON OF DATA FOR SYNTHETIC AND NATURAL α-D-GALACTOPYRANOSYLPINITOLS[a]

	Natural product[2]	*Compound* **9**	*Compound* **11**
$[\alpha]_D$ (water) (degrees)	+174[b]	+174	+153
R_{GLC} (t.l.c.; BuOH–MeOH–H_2O, 2:1:1)	0.90	0.90	0.84
R_{GLC} (t.l.c.; Me_2CO–H_2O, 9:1)	0.50	0.50	0.37
R_F (t.l.c.; BuOH–Me_2CO–H_2O, 3:3:1)	0.34	0.34	0.28

[a]For n.m.r. data, see Table III. [b]Measured on the same polarimeter as for **9** and **11**, with *c* 0.1.

Eluted third was *1D-1,5-di-O-benzoyl-3-O-benzyl-4-O-methyl*-chiro-*inositol* (**5**: 200 mg, 16%), $[\alpha]_D$ +39° (*c* 0.9, chloroform).

Anal. Calc. for $C_{28}H_{28}O_8$: C, 68.3; H, 5.73. Found: C, 68.1; H, 5.61.

The isomers **4** and **5** were difficult to separate. Losses of material occurred during repeated chromatography to obtain each isomer in a pure state.

In order to facilitate n.m.r. assignments, a portion of **5** was acetylated with acetic anhydride in pyridine and worked-up as usual, to give **5a**.

Eluted fourth was *1D-2,6-di-O-benzoyl-3-O-benzyl-4-O-methyl*-chiro-*inositol* (**6**: 210 mg, 17%), $[\alpha]_D$ +12° (*c* 0.9, chloroform).

Anal. Calc. for $C_{28}H_{28}O_8$: C, 68.3: H, 5.73. Found: C, 68.0; H, 5.66. A portion of **6** was converted into the acetate **6a**.

1D-3-O-Benzyl-4-O-methyl-2-O-(2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl)-chiro-*inositol* (**8**). — A mixture of **5** (200 mg, 0.41 mmol), 2,3,4,6-tetra-*O*-benzyl-1-*O*-(*N*-methylacetimidoyl)-β-D-galactopyranose (**7**) (450 mg, 0.77 mmol), powdered 4Å molecular sieve (1.0 g), and toluene-*p*-sulfonic acid (75 mg) in benzene (10 ml) was stirred at room temperature for 48 h. Triethylamine (0.3 ml) was added, and the mixture was diluted with chloroform, filtered, and concentrated. A solution of the residue in chloroform was washed with aqueous sodium hydrogencarbonate and water, dried (Na_2SO_4), filtered, and concentrated. The residue was debenzoylated with methanolic sodium methoxide, and the crude **7** thus obtained was purified by column chromatography (toluene–ethyl acetate, 1:1), to give **8** (140 mg, 43%), m.p. 132–133° (from ether–light petroleum), $[\alpha]_D$ +73° (*c* 0.9, chloroform).

Anal. Calc. for $C_{48}H_{54}O_{11}$: C, 71.4; H, 6.75. Found: C, 71.4; H, 6.79.

A portion of **8** was acetylated with acetic anhydride and pyridine, to yield the triacetate **8a**. ^{1}H-N.m.r. data ($CDCl_3$): δ 1.84, 1.93, 2.03 (3 s, each 3 H, 3 OAc), 3.55 (s, 3 H, OMe), 5.11 (dd, 1 H, H-5), 5.26 (t, 1 H, H-6), 5.44 (t, 1 H, H-1); $J_{1,2}$ 3, $J_{1,6}$ 3, $J_{4,5}$ 10, $J_{5,6}$ 3 Hz.

1D-2-O-(α-D-Galactopyranosyl)-4-O-methyl-chiro-*inositol* (**9**). — Catalytic hydrogenolysis of **8** (100 mg) over 10% palladium-on-carbon (150 mg) in acetic acid (25 ml), followed by filtration and concentration, yielded **9**, $[\alpha]_D$ +174° (*c* 0.2, water).

1D-3-O-Benzyl-4-O-methyl-5-O-(2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl)-

chiro-*inositol* (**10**). — Compound **6** (200 mg, 0.41 mmol) was galactosylated, and the product was debenzoylated and worked-up as described in the preparation of **9**. The product **10** (130 mg, 40%) had $[\alpha]_D$ +71° (*c* 0.9, chloroform).

Anal. Calc. for $C_{48}H_{54}O_{11}$: C, 71.4; H, 6.75. Found: C, 71.1; H, 6.57.

A portion of **10** was acetylated with acetic anhydride and pyridine, to yield the triacetate **10a**. ^{1}H-N.m.r. data ($CDCl_3$): δ 1.84, 1.93, and 2.02 (3 s, each 3 H, 3 OAc), 3.55 (s, 3 H, OMe), 5.11 (dd, 1 H, H-2), 5.27 (t, 1 H, H-1), 5.44 (t, 1 H, H-6); $J_{1,2}$ 3, $J_{1,6}$ 3, $J_{2,3}$ 9, $J_{5,6}$ 3 Hz.

*1*D-*5*-O-(α-D-*Galactopyranosyl*)-*4*-O-*methyl*-chiro-*inositol* (**11**). — Catalytic hydrogenolysis of **10**, as described in the preparation of **9**, afforded **11**, $[\alpha]_D$ +153° (*c* 0.2, water).

ACKNOWLEDGMENTS

We thank Professors H. Erdtman and G. N. Richards for generous gifts of pinitol and galactosylpinitol[2], respectively, Professor B. Lindberg for his interest, and the Swedish Natural Research Council for financial support.

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