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SYNTHESIS OF 5-*O*-METHYL-D-GALACTOFURANOSE

MARCOS L. SZNAIDMAN, ALICIA FERNÁNDEZ CIRELLI*, AND ROSA M. DE LEDERKREMER*
Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón II, 1428 Buenos Aires (Argentina)

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ABSTRACT

5-*O*-Methyl-D-galactofuranose (**7**) was synthesized, for the first time, in five steps from D-galactono-1,4-lactone (**1**) in good overall yield. Tritylation and further acetylation of **1** gave 2,3,5-tri-*O*-acetyl-6-*O*-trityl-D-galactono-1,4-lactone (**2**); prolonged acetylation caused elimination to form 2,5-di-*O*-acetyl-3-deoxy-6-*O*-trityl-D-*threo*-hex-2-enono-1,4-lactone. Detritylation of **2** with $BF_3 \cdot Et_2O$ occurred with acetyl migration and afforded 2,3,6-tri-*O*-acetyl-D-galactono-1,4-lactone (**4**). Methylation of **4** with CH_2N_2–$BF_3 \cdot Et_2O$ gave 5-*O*-methyl-2,3,6-tri-*O*-acetyl-D-galactono-1,4-lactone. Subsequent reduction by disiamylborane followed by controlled deacetylation gave crystalline **7**. The ^1H- and ^{13}C-n.m.r. spectra of **7** indicated a 1:1.3 ratio of the α and β furanose anomers.

INTRODUCTION

Aldono-1,4-lactones are useful starting materials for the synthesis of furanoses[1]. We have previously described the synthesis of furanose derivatives of deoxy sugars *via* β-elimination reactions occurring on benzoylation of aldonolactones[2–4].

We report here the first synthesis of 5-*O*-methyl-D-galactofuranose, starting from the commercially available D-galactono-1,4-lactone (**1**). In the aldohexose series, only 5-*O*-methyl-D-glucofuranose[5–7] and 5-*O*-methyl-D-mannofuranose[8,9] have been synthesized; specific methods were used that take into account the relative configuration of the chiral centers for each monosaccharide. These multistep procedures are tedious and result in poor overall yields. The advantage of the route here described is its general potential applicability to the synthesis of any 5-*O*-methylaldohexofuranose.

RESULTS AND DISCUSSION

Tritylation of D-galactono-1,4-lactone (**1**) with chlorotriphenylmethane in

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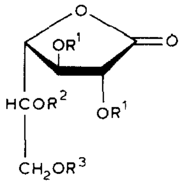
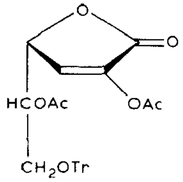
pyridine for 48 h at room temperature, followed by acetylation with acetic anhydride for 8 h, yielded 2,3,5-tri-*O*-acetyl-6-*O*-trityl-D-galactono-1,4-lactone (**2**) as the main product. Compound **2** was obtained as an amorphous solid in 75% yield and was characterized on the basis of its spectroscopic properties. Comparison of the ^{1}H-n.m.r. data for compound **2** with those reported for 2,3,5,6-tetra-*O*-acetyl-D-galactono-1,4-lactone[10] (**8**) (Table I) show that the signals of H-6 and 6′ are shifted 0.93 p.p.m. and H-5 is shifted 0.18 p.p.m. to lower field in the latter compound; this is attributable to the greater electronegativity of the acetyl group.



1 $R^1 = R^2 = R^3 = H$
2 $R^1 = R^2 = Ac, R^3 = Tr$
4 $R^1 = R^3 = Ac, R^2 = H$
5 $R^1 = R^3 = Ac, R^2 = Me$
8 $R^1 = R^2 = R^3 = Ac$



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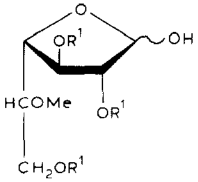

6 $R^1 = Ac$
7 $R^1 = H$

The chemical shifts for C-2,3,4,5, and 6 were assigned by comparison with the ^{13}C-n.m.r. spectrum of the fully acetylated compound[11] **8** (Table II). Replacement of an acetyl by a trityl group caused a downfield shift of C-5 in compound **2**.

When the acetylation time was prolonged to 48 h, an unsaturated, crystalline lactone was obtained in 9% yield that was characterized as 2,5-di-*O*-acetyl-3-deoxy-6-*O*-trityl-D-*threo*-hex-2-enono-1,4-lactone (**3**). Its i.r. spectrum showed carbonyl absorption at 1780 (α,β-unsaturated 1,4-lactone) and 1740 cm^{-1} (acetyl

TABLE I

^{1}H-N M R CHEMICAL SHIFTS AND COUPLING CONSTANTS (Hz) FOR COMPOUNDS **2–5** AND **8**

Compound	*H-2* $(J_{2,3})$	*H-3* $(J_{3,4})$	*H-4* $(J_{4,5})$	*H-5* $(J_{5,6}, J_{5,6})$	*H-6 H-6′* $(J_{6,6'})$
2	5.57d	5.37t	4.67q	5.14m	3.37m
	(6.5)	(6.5)	(2.5)		
3		7.02d	5.42q	5.12m	3.50m
		(2.0)	(3.0)	(7.0, 9.0)	(11.0)
4	5.68d	5.38t	4.40m	3.80m	4.20m
	(5.0)	(5.0)			
5		5.70–5.59m	4.45q	3.63m	4.36–4.19m
		(5.9)	(2.8)		
8[a]	5.64	5.44	4.60	5.32	4.30

[a] Ref. 10.

TABLE II

^{13}C-N M R CHEMICAL SHIFTS OF COMPOUNDS **2–5** AND **7–10**

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Ref.*
2	168.0	72.1	72.1	77.3	69.4	61.2	
3	166.0	138.4	130.5	77.6	70.9	62.0	
4	168.6	72.1[a]	72.4[a]	79.2	67.6	64.3	
5	168.3	72.0[a]	72.8[a]	79.2	76.7	61.8	
8	170.0	71.8[a]	71.9[a]	77.1	68.0	61.3	10
7(α)	95.9	77.2	75.4	80.9	83.5	60.5	
7(β)	101.7	82 3[a]	76.9	81.5[a]	82.3[a]	60.9	
9(α)	95.8	77.1	75.1	81.6		63.3	16
9(β)	101.8	82.2	76.6	82.8	71.5	63.6	16
10	109.0	81.8	77.8	83.4	81.8	60.9	18

[a] The assignments may be interchanged.

C=O). The ^{1}H-n.m.r. spectrum of **3** (Table I) was in accordance with the postulated structure. The vinylic proton (H-3) resonated as a doublet at 7.02 p.p.m. This unusual deshielding may be explained in terms of conjugation between the double bond and the carbonyl group. According, C-2 and C-3 resonated at 138.4 and 130.5 p.p.m., respectively, in the ^{13}C-n.m.r. spectrum (Table II).

The α,β-unsaturated lactone **3** is formed by elimination of the acetyloxy group β to the lactone carbonyl. Similar eliminations in aldono-1,4- and 1,5-lactones have been extensively studied in our laboratory[2,3,12,13].

Detritylation of **2** with boron trifluoride etherate occurred with acetyl migration from O-5 to O-6 to give 2,3,6-tri-*O*-acetyl-D-galactono-1,4-lactone (**4**) in 85% yield. Acyl migrations to primary hydroxyl groups are favored and have been reported on detritylation in protic media[14]. The spectroscopic data accord with the postulated structure. The signal for H-5 was the only one shifted upfield in comparison with the spectra for compounds **2** and **8**. In the ^{13}C-n.m.r. spectrum, C-4 and C-6 are shifted downfield (Table II) in comparison with these signals in compound **8**, as would be expected for a free hydroxyl group in C-5 of **4**.

Methylation of **4** with diazomethane and boron trifluoride etherate, conditions reported as preventing acyl migrations[15], gave 2,3,6-tri-*O*-acetyl-5-*O*-methyl-D-galactono-1,4-lactone (**5**). The ^{1}H-n.m.r. spectra for compounds **4** and **5** are very similar (Table I). In the ^{13}C-n.m.r. spectrum (Table II), the C-5 signal was unambiguously assigned by selective irradiation at 3.63 p.p.m. (H-5). It is deshielded by 9.1 p.p.m. in comparison with the hydroxylated compound **4**. The mass spectrum further confirmed methylation at position 5. The primary fragment at *m/z* 117, which corresponds to cleavage between C-5 and the ring, was 84.2% of the base peak.

Compound **5** was reduced with disiamylborane in tetrahydrofuran to afford 2,3,6-tri-*O*-acetyl-5-*O*-methyl-D-galactofuranose (**6**) as a syrup in 70% yield. The ^{1}H-n.m.r. spectrum was difficult to assign because of the presence of both anomers of **6** in approximately equal amounts, as shown by the OCH_3 signals at 3.69 and 3.58 p.p.m. The anomeric carbon atoms in the ^{13}C-n.m.r. spectrum were assigned by taking into account that a 1,2-*trans* relationship in furanose rings results in a downfield shift of the signals for the corresponding carbon atoms. In the β anomer, C-1 resonates at 100.3 p.p.m. whereas in the α anomer, C-1 resonates at 95.0 p.p.m., in accordance with data in the literature for related compounds[16]. The signals for C-4 and C-6 were assigned by selective irradiation at 4.1 p.p.m. The remaining carbon atoms could not be unambiguously assigned.

Deacetylation of **6** with sodium methoxide under controlled conditions gave crystalline 5-*O*-methyl-D-galactofuranose (**7**). In the ^{1}H-n.m.r. spectrum, the signals at 5.18 ($J_{1,2}$ 4.5 Hz) and 5.12 p.p.m. ($J_{1,2}$ 2.9) were assigned to the α and β anomers, respectively (ratio 1:1.3), by comparison with values reported for related aldofuranoses[17]. Even in a highly resolved ^{1}H-n.m.r. spectrum (500 MHz), no signal was evident downfield of 5.3 p.p.m. indicating that if the *aldehydo* form is present in the equilibrium, the amount is too small to be detected. In the anomeric region of the ^{13}C-n.m.r. spectrum, the signals at 101.7 (β) and 95.9 p.p.m. (α) indicated the preponderance of the β anomer in the mixture. The remaining carbon resonances were assigned by comparison with spectral data for α-D- and β-D-galactofuranose[16] (**9**) and methyl 5-*O*-methyl-β-D-galactofuranoside[18] (**10**) (Table II). As expected, methylation at O-5 causes deshielding of C-5 (7–11 p.p.m. to lower field) and an upfield shift of the β carbon atoms (C-4 and C-6).

This is the first report of the synthesis of 5-*O*-methyl-D-galactofuranose. Methyl 5-*O*-methyl-D-galactofuranoside (**10**) was previously obtained as a mixture of anomers, starting from methyl 2,3-di-*O*-benzyl-6-*O*-trityl-α,β-D-galactofuranoside[19]. Although acid hydrolysis of **10** would have readily afforded 5-*O*-methyl-D-galactofuranose, the authors did not describe this sugar.

EXPERIMENTAL

General. — Evaporations were conducted under diminished pressure at a bath temperature below 60°. Melting points were determined with a Fisher–Johns apparatus and are uncorrected. Optical rotations were recorded with a Perkin–Elmer 141 polarimeter, and i.r. spectra with a Perkin–Elmer 421 spectrophotometer. The ^{1}H- and ^{13}C-n.m.r. spectra were determined with a Varian XL-100 spectrometer. Tetramethylsilane was used as the internal reference for solutions in chloroform-*d* (compounds **2**–**6**) and 1,4-dioxane was used as the external standard when D_2O was used (δ_C 67.4 p.p.m. downfield from Me_4Si). The apparent coupling-constants (Hz) reported are the directly observed line-spacings. Signal assignments in ^{13}C-n.m.r. spectra were made on the basis of selective decoupling experiments or by comparison with literature data. A Nicolet 500-MHz spectrometer was used for the ^{1}H-n.m.r. spectrum of compound **7**. The mass spectrum was obtained with a Varian MAT CH 7 spectrometer coupled to a Varian MAT data-system 166. T.l.c. was performed on Silica Gel G (Merck) with: (*A*) 9:1 benzene–

ethyl acetate; (*B*) 19:1 chloroform–methanol; or (*C*) 4:1 chloroform–methanol as the mobile phase; detection was effected with iodine vapor. Paper chromatography was conducted by the descending method on Whatman no. 1 paper with: (*D*) 6:4:3 1-butanol–pyridine–water. Detection was effected with (*i*) silver nitrate–sodium hydroxide[20] and (*ii*) *p*-anisidine hydrochloride[21].

*2,3,5-Tri-O-acetyl-6-O-trityl-*D*-galactono-1,4-lactone* (**2**). — D-Galactono-1,4-lactone (**1**, 4.86 g, 27.3 mmol) was dissolved in anhydrous pyridine (30 mL) at room temperature and chlorotriphenylmethane (8.37 g, 30.0 mmol) was slowly added. The mixture was kept for 48 h at room temperature, diluted with anhydrous pyridine (45 mL), cooled to 0°, and freshly distilled acetic anhydride (45 mL) was added dropwise with stirring. After 8 h, the solution was poured into 600 mL of ice–water. The product was extracted with dichloromethane, and the extract was washed successively with saturated aqueous sodium hydrogensulfate, saturated aqueous hydrogencarbonate, and water until pH 7 had been reached, dried (magnesium sulfate), and evaporated. T.l.c. of the syrup showed a main product (R_F 0.45), together with a minor one (R_F 0.48, solvent *A*). The mixture was dissolved in hot ethanol and on cooling a chromatographically homogeneous, amorphous solid separated, which could not be induced to crystallize (11.2 g, 75%). It was characterized as 2,3,5-tri-*O*-acetyl-6-*O*-trityl-D-galactono-1,4-lactone (**2**); $[\alpha]_D^{20}$ −38.7° (*c* 1.0, chloroform); ν_{max}^{Nujol} 1810 (1,4-lactone CO), 1750 (acetyl CO), 770, 750, and 710 cm^{-1} (aromatic C-H); ^{1}H-n.m.r., δ 7.5–7.2 (m, 15 H, aromatic H), 2.13 (s, CH_3CO), 2.10 (s, CH_3CO), and 2.08 (s, CH_3CO) (for other proton signals, see Table I); ^{13}C-n.m.r., δ 169.4, 169.3, 169.0 (CH$_3$*C*O), 143.1 (C-1 Ph), 128.3–127.1 (aromatic C), 87.2 (*C*Ph$_3$), 20.6, 20.4, and 20.2 (*C*H$_3$CO) (for other carbon resonances, see Table II).

Anal. Calc. for $C_{31}H_{30}O_9$: C, 68.12; H, 5.53. Found: C, 68.15; H, 5.63.

*2,5-Di-O-acetyl-3-deoxy-6-O-trityl-*D-threo-*hex-2-enono-1,4-lactone* (**3**). — D-Galactono-1,4-lactone (**1**, Pfanstiehl) was treated as before, but the acetylation time was prolonged to 48 h at room temperature. T.l.c. of the mixture showed an increased proportion of the product of higher mobility (R_F 0.48, solvent *A*). This compound was separated from the major one (compound **2**) by column chromatography on Silica Gel H (Merck) (25 × 5 cm), using 19:1 benzene–ethyl acetate as eluent. Compound **3** crystallized from ethanol (0.250 g, 9% yield); m.p. 135–137°, $[\alpha]_D^{20}$ −8.1 (*c* 1.0, chloroform). It was characterized on the basis of its spectroscopic features: ν_{max}^{Nujol} 1780 (α,β-unsaturated 1,4-lactone CO), 1740 (acetyl CO), and 760 and 700 cm^{-1} (aromatic C-H), ^{1}H-n.m.r., δ 7.6–7.2 (m, 15 H, aromatic H), 2.28 (s, CH_3CO), and 2.18 (s, CH_3CO) (for other proton signals, see Table I); ^{13}C-n.m.r., δ 169.7 and 166.5 (acetyl *C*O), 143.1 (C-1 Ph), 128.3–127.1 (aromatic C), 87.1 (*C*Ph$_3$), and 20.6 (*C*H$_3$CO) (for other carbon resonances, see Table II).

Anal. Calc. for $C_{29}H_{26}O_7$: C, 71.59; H, 5.39. Found: C, 71.58; H, 5.56.

*2,3,6-Tri-O-acetyl-*D*-galactono-1,4-lactone* (**4**). — Detritylation of compound **2** was performed according to the method described by Dax *et al.*[22]. Boron trifluoride etherate (0.12 mL, 1 mmol) and methanol (0.4 mL) were added to a solution of **2** (0.55 g, 1 mmol) in dichloromethane (40 mL) and the mixture was kept at room temperature until no more starting material was observed by t.l.c. (~1 h). Water (3 × 3 mL) was added and the organic layer was separated, dried over magnesium sulfate, and evaporated to dryness. T.l.c. of the syrup showed a main product (R_F 0.40, solvent *B*), and triphenylmethanol. It was purified by successive washings with hot cyclohexane to give a homogeneous product; yield 0.26 g (85%) which could not be induced to crystallize, and was characterized as 2,3,6-tri-*O*-acetyl-D-galactono-1,4-lactone (**4**); $[\alpha]_D^{20}$ −28.7° (*c* 1.0, chloroform); ν_{max}^{Nujol} 3450 (OH), 1800 (1,4-lactone CO), and 1750 cm^{-1} (acetyl CO); ^{1}H-n.m.r., δ 3.40 (broad, disappeared on deuteration, O*H*), 2.20 (s, CH_3CO), 2.16 (s, CH_3CO), and 2.14 (s, CH_3CO) (for other proton signals, see Table I); ^{13}C-n.m.r., δ 171.0, 170.1 and 169.6 (CH_3CO), 20.8, 20.6, and 20.4 (CH_3CO) (for other carbon resonances, see Table II).

Anal. Calc. for $C_{12}H_{16}O_9$: C, 47.37; H, 5.30. Found: C, 47.41; H, 5.55.

2,3,6-Tri-O-acetyl-5-O-methyl-D-galactono-1,4-lactone (**5**). — To a solution of **4** (0.90 g) in dichloromethane (4.0 mL) boron trifluoride etherate (0.04 mL) was added. The temperature was kept at −5° with external cooling and a solution of CH_2N_2 in dichloromethane was added dropwise with stirring until the yellow color persisted. After 30 min at −5°, the precipitated polymethylene was filtered off and the filtrate successively washed with saturated aqueous sodium hydrogencarbonate and water to neutrality. The syrup (0.9 g) obtained on evaporation showed by t.l.c. a main product (R_F 0.25, solvent *A*) that was purified by column chromatography on Silica Gel H (Merck) with 4:1 benzene–ethyl acetate as eluent. It could not be induced to crystallize and was characterized as 2,3,6-tri-*O*-acetyl-5-*O*-methyl-D-galactono-1,4-lactone (**5**); yield 84%; $[\alpha]_D^{20}$ −38.0° (*c* 1.0, chloroform); ν_{max}^{Nujol} 1800 (1,4-lactone CO) and 1750 cm^{-1} (acetyl CO); ^{1}H-n.m.r., δ 3.55 (s, OCH_3), 2.19 (s, CH_3CO), 2.13 (s, CH_3CO), and 2.10 (s, CH_3CO) (for other proton signals, see Table I); ^{13}C-n.m.r., δ 170.4, 170.0, 169.5 (CH_3CO), 59.4 (OCH_3), 20.7, 20.6, and 20.4 (CH_3CO) (for other carbon resonances, see Table II); *m/z* (%): 287 (4.0), 259 (4.1), 245 (2.2), 243 (6.7), 201 (2.2), 185 (13.6), 145 (9.0), 143 (17.5), 142 (8.6), 141 (1.3), 117 (84.2), 115 (9.9), 103 (12.7), 100 (11.5), 99 (5.4), 87 (14.1), 73 (4.6), 71 (4.5), and 43 (100.0).

Anal. Calc. for $C_{13}H_{18}O_9$: C, 49.06; H, 5.70. Found: C, 49.15; H, 5.89.

2,3,6-Tri-O-acetyl-5-O-methyl-D-galactofuranose (**6**). — Compound **5** was reduced with disiamylborane according to the procedure described by Kohn *et al.*[1]. To a solution containing 6 mmol of freshly prepared bis-(3-methyl-2-butyl)borane under a nitrogen atmosphere, 0.40 g (1.2 mmol) of **5** in tetrahydrofuran was added. The mixture was stirred for 20 h at room temperature and then treated as previously described[12]. The resulting syrup (0.38 g) showed by t.l.c. a main product (R_F 0.15, solvent *A*) that was purified by column chromatography on Silica Gel H (Merck) with 49:1 chloroform–methanol as eluent. The resulting syrup (0.28 g, 70% yield) was chromatographically homogeneous and was characterized as 2,3,6-tri-*O*-acetyl-5-*O*-methyl-D-galactofuranose; $[\alpha]_D^{20}$ −20.9° (*c* 1.0, chloroform). ν_{max}^{Nujol} 3400 (OH) and 1740 cm^{-1} (acetyl CO); ^{1}H-n.m.r., δ 5.48–5.02 (m, H-1,2,3), 4.38–4.03 (m, H-4,6,6′), 3.69 (s, OCH_3), 3.58 (s, OCH_3), 3.45 (m, H-5), and 2.18–2.02 (superposed singlets, CH_3CO); ^{13}C-n.m.r., δ 170.7, 170.5, 170.3, 170.1, and 169.9 (CH_3CO), 100.3 (C-1 β), 95.0 (C-1 α), 82.3 (C-2 β), 81.5 (C-4 α and β), 77.9, 77.8, 77.4, 76.8, and 76.6 (C-2 α, C-3 α and β, C-5 α and β), 63.1 and 62.8 (C-6 α and β), 59.8 and 59.4 (OCH_3, α and β), and 20.8 and 20.6 (CH_3CO).

Anal. Calc. for $C_{13}H_{20}O_9$: C, 48.75; H, 6.29. Found: C, 48.98; H, 6.56.

*5-O-Methyl-*D*-galactofuranose* (**7**). — Compound **6** (0.20 g) was dissolved in chloroform (5.0 mL) and treated with 0.5M sodium methoxide in methanol (5.0 mL). After stirring for 1 h at 0°, water was added, and the organic layer was separated and extracted three times with water. The aqueous solution, freed from methyl benzoate, was decationized with Dowex 50 W (H^+) resin and evaporated to a syrup (0.12 g). T.l.c. showed a main product (R_F 0.30, solvent *C*) that was purified by column chromatography on Silica Gel H (Merck) with 4:1 chloroform–methanol as eluent. Paper chromatography showed only one spot ($R_{3\text{-}O\text{-methylglucose}}$ 1.19, solvent *D*, reagents *i* and *ii*). It crystallized from 1-propanol (0.08 g, 66%) and was characterized as 5-*O*-methyl-D-galactofuranose (**7**); m.p. 135–137°, $[\alpha]_D^{20}$ $-15.7°$ (*c* 0.5, water); ^{1}H-n.m.r. (D_2O, 500 MHz): δ 5.18 (d, $J_{1,2}$ 4.5, H-1α), 5.12 (d, $J_{1,2}$ 2.9, H-1β), 3.97 (m, H-2,3,4 α and β), 3.65 (m, H-6,6′ α and β), 3.433 (s, $OCH_3\alpha$), 3.431 (s, OCH_3 β), and 3.40 (m, H-5 α and β); ^{13}C-n.m.r., δ 59.4 (OCH_3 α and β) (for other carbon resonances, see Table II).

Anal. Calc. for $C_7H_{14}O_6$: C, 43.30; H, 7.27. Found: C, 43.37; H, 7.23.

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