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Enantiospecific Syntheses of (3*S*,4*R*)- and (3*S*,4*R*,7*S*)-Diastereoisomers of Goniofufurone

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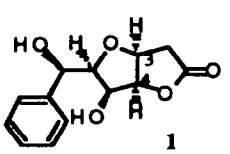
Abstract: D-Mannose has been converted by six sequential reactions (acetonation, Wittig-intramolecular Michael reaction, selective deacetonation, glycol cleavage oxidation and Grignard reaction) into the methyl esters **9** and **10** which underwent a de-isopropylidenation reaction with concommitant lactonisation to give the (3*S*,4*R*)- and (3*S*,4*R*,7*S*)-diastereoisomers of goniofufurone **1** and **2**.

We have long-term interest in the fabrication of heavily oxygenated lactones as potential antitumour agents from sugars[1] and recently we described the total syntheses (from D-*glycero*-D-*gulo*-heptono-γ-lactone) of several styryllactones which were isolated from the ethanolic extracts of the stem bark of *Goniothalamus giganteus* Hook. f., Thomas (Annonaceae).[2,3] All these styryllactones, (+)-goniofufurone,[4] (-)-goniotriol,[5,4g] (-)-8-acetylgoniotriol,[5,4g] and (+)-goniopypyrone[6,4g] have been successfully synthesised firstly by us and then by others. It is noteworthy that whereas goniofufurone shows significant cytotoxic activities toward several human tumour cell lines, 7-*epi*-goniofufurone (sugar numbering) is only weakly bioactive.[2,3] This finding prompted us to prepare configurational analogues of goniofufurone for biological evaluation as selective antitumour agents. This paper now reports, starting from D-mannose, short, facile and enantiospecific syntheses of (3*S*,4*R*)- and (3*S*,4*R*,7*S*)-diastereoisomers of goniofufurone **1** and **2**.



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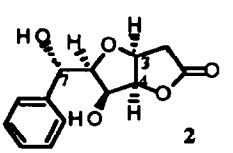
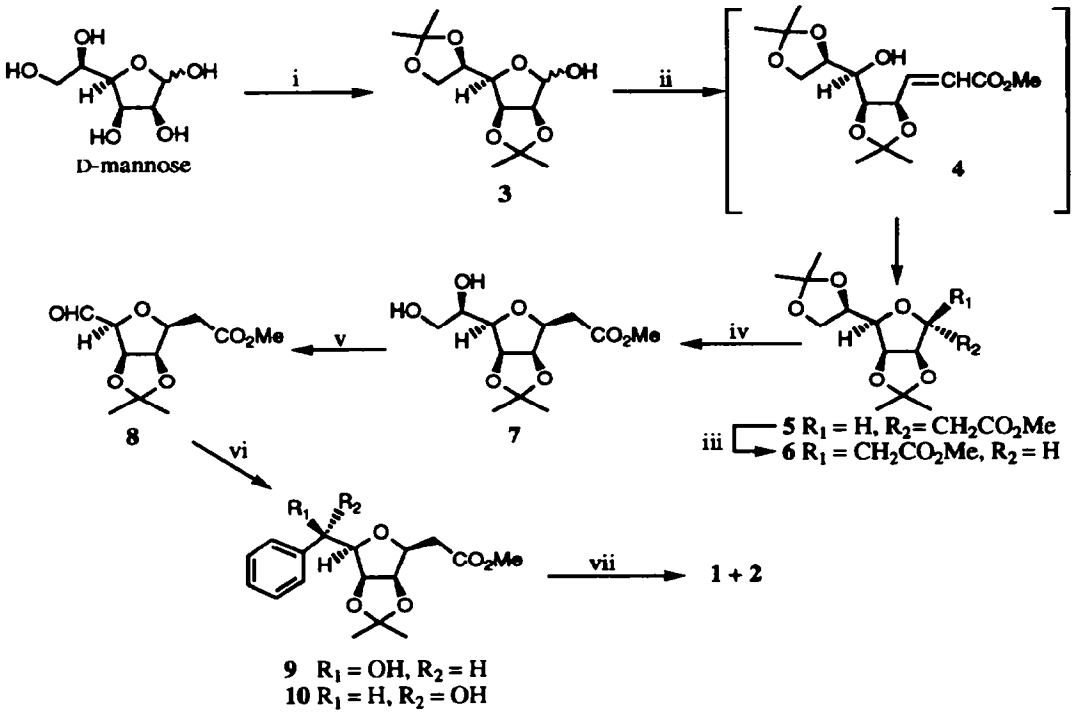
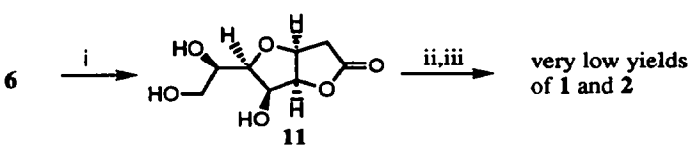


2

The strategy for our previous construction of goniofufurone and 7-*epi*-goniofufurone from D-*glycero*-D-*gulo*-heptono-γ-lactone (D-glucoheptono-γ-lactone) involved three key reactions in sequence namely the PhMgBr Grignard reaction, Wittig reaction and the intramolecular Michael reaction.[4c] The application of this



Scheme 1. *Reagents and conditions* : i, $Me_2C{=}O$, *p*-TsOH, reflux (85%); ii, $Ph_3P{=}CHCO_2Me$, MeCN, reflux (combined 93%, **5** : **6** = 1 : 1); iii, NaOMe, MeOH, r.t. (combined 93%, **5** : **6** = 2 : 5); iv, HOAc-H_2O, r.t. (92%); v, $NaIO_4$, MeOH-H_2O, r.t.; vi, PhMgBr, THF, 0 °C (52% from **7**, **9** : **10** = 1 : 1, inseparable); vii, HOAc-H_2O, reflux (combined 80%, separable on alumina)



Scheme 2. *Reagents and conditions* : i, TFA-H_2O-CH_2Cl_2, r.t. (81%); ii, $NaIO_4$, MeOH-H_2O, r.t.; iii, PhMgBr, THF, O °C.

strategy has now been demonstrated by obtaining diastereoisomers **1** and **2** from D-mannose, although the sequence of events is different. Taking advantage of the unblocked C-1 lactol function in diacetone-D-mannose **3**, the [3.3.0] bicyclic ring system in the target molecules can be assembled *via* a Wittig-intramolecular Michael-hydrolysis sequence. A final PhMgBr Grignard reaction would then complete the syntheses of **1** and **2**.

The route to goniofufurone analogues **1** and **2** is illustrated in Scheme 1. The crystalline diacetone-D-mannose **3**[7] was readily available from D-mannose in 85% yield employing milder conditions (tosic acid as the catalyst). The lactol **3** reacted with (methoxycarbonyl)methylenetriphenylphosphorane in refluxing acetonitrile to form an intermediate enoate **4** which then underwent a spontaneous intramolecular Michael-type ring closure, affording a mixture of α- and β-*C*-glycosides **5** and **6** in a ratio of *ca.* 1 : 1.[8] The β-*C*-glycoside **6** would afford the desired [3.3.0] bicyclic ring system upon acidic removal of the acetonide blocking groups followed by lactonisation whereas the α-*C*-glycoside **5** would not lactonise due to steric reasons. Treatment of the mixture of *C*-glycosides with NaOMe in MeOH caused equilibration *via* a ring-opening and ring-closure mechanism to give the β-*C*-glycoside **6** as the major product. Although all the substituents on the furanoid ring in **6** are *cis*-disposed, the β-*C*-glycoside **6** was assigned as the thermodynamic product.[8] In this work, molecular mechanics calcualtions using the MM2 force field of Allinger[9] showed that the E_{steric} of **5** was *ca.* 1 kcal mol^{-1} less than that of **6**. Thus compound **6** as a free molecule may not be theromodynamically more stable than **5**. Selective hydrolysis of the terminal isopropylidene ring in **6** proceeded smoothly in aqueous acetic acid to give the diol **7** in an excellent yield (92%). Glycol cleavage oxidation[10] of the diol moiety in **7** with sodium metaperiodate in aqueous methanol followed by immediate reaction of the liberated aldehyde with PhMgBr Grignard reaction in THF, afforded a mixture of inseparable benzyl alcohols **9** and **10** (ratio *ca.* 1 : 1) in an overall yield of 52%. Hydrolysis of the remaining isopropylidene group in **9** and **10** (as a mixture) with aqueous acetic acid occurred with concomitant lactonisation to give the target molecules **1** and **2**, separable by alumina chromatography. By comparison of the ^{1}H NMR spectral data of **1** and **2** with those of goniofufurone and 7-*epi*-goniofufurone, the more polar lactone was tentatively assigned as the (3*S*,4*R*)-diastereoisomer **1** and the less polar lactone as the (3*S*,4*R*,7*S*)-diastereoisomers of goniofufurone **2**.

A less efficient route from **6** towards the target compounds **1** and **2** is illustrated in Scheme 2. Hydrolysis of the remaining isopropylidene blocking group in **6** proceeded with concomitant lactonisation to give the triol **11** in good yields. However, glycol cleavage oxidation[10] followed by immediate reaction of the liberated aldehyde with PhMgBr gave very low yields of **1** and **2**.

In conclusion, this paper reports short syntheses of two goniofufurone diastereoisomers from D-mannose in seven steps. The antitumour activities of the new lactones will be reported elsewhere.

Experimental Section

Melting points were recorded on a Peichert apparatus and are uncorrected. ^{1}H NMR spectra were measured on a Brucker WM250 (250-MHz) spectrometer in with tetramethylsilane as an internal standard unless otherwise noted. IR spectra were recorded with a Nicolet 205 FT-IR spectrometer. Mass spectra were taken on a VG Micromass 7070F mass spectrometer. Specific rotations were measured with a JASCO DIP-300 digital polarimeter. Elemental analyses were carried out at the Shanghai Institute of Organic Chemistry, Academic Sinica, China. TLC was performed on aluminum precoated with silica gel $60F_{254}$ and compounds were visualised with a spray of 5% w/v dodecamolybdophosphoric acid in ethanol and subsequent heating. Flash

chromatography was performed on silica gel (230-400 mesh). THF was distilled from sodium and benzophenone under nitrogen.

2,3:5,6-*Di*-O-*isopopylidene*-α-D-mannofuranose 3.[7]—*p*-Toluenesulfonic acid monohydrate (0.25 g, 1.31 mmol) was added in one portion to a suspension of D-mannose (12.5 g, 0.069 mol) in dry acetone (400 cm^3). The suspension was then refluxed at 60–70 °C for 24 h. The solution was stirred with potassium carbonate (1.0 g) at room temperature until pH 8. The mixture was filtered through Celite and evaporation of solvent *in vacuo* from the filtrate gave a white solid. The white solid was dissolved in dichloromethane and was filtered through a bed of silica topped with Celite. Evaporation of solvent *in vacuo* afforded the *diacetonide* **3** (15.4 g, 85%) as a white solid. Recrystallization from diethyl ether-hexane gave **3** as colorless crystals, m.p. 119—121 °C (lit.,[7] m.p. 120 °C); R_f 0.50 [diethyl ether-hexane (3 : 2 v/v)]; $[\alpha]_D^{24}$ + 11.8 (*c* 1.3 in $CHCl_3$ for 45 min) {lit.,[7] $[\alpha]_D^{20}$ + 10 (*c* 1.9 in $CHCl_3$, 45 min)}; ν_{max}/cm^{-1} 3431 (OH); δ_H ($CDCl_3$) 1.33 (3 H, s, Me), 1.38 (3 H, s, Me), 1.46 (6 H, s, 2 × Me), 3.00 (1 H, br s, OH), 4.05 (1 H, dd, *J* 5.1 and 8.6, 6-Hb), 4.10 (1 H, dd, *J* 6.0 and 8.6, 6-Ha), 4.19 (1 H, dd, *J* 3.7 and 7.2, 4-H), 4.37–4.45 (1 H, m, 5-H), 4.62 (1 H, d, *J* 5.9, 2-H), 4.82 (1 H, dd, *J* 3.7 and 5.9, 3-H), 5.38 (1 H, br s, 1-H); *m/z* (EI) 101 (100%, $C_5O_2H_9^+$), 187 (19.68, $M^+ - Me - C_3H_6O$), 245 (66.61, $M^+ - Me$).

Methyl 3,6-*anhydro*-2-*deoxy*-4,5:7,8-*di*-O-*isopropylidene*-D-glycero-D-talo-*octanoate* 5 and Methyl 3,6-*anhydro*-2-*deoxy*-4,5:7,8-*di*-O-*isopropylidene*-D-glycero-D-galacto-*octanoate* 6.[8]—(Methoxycarbonyl)methylenetriphenylphosphorane (11.6 g, 0.035 mol) was added to a stirred suspension of the diacetonide **3** (6.0 g, 0.023 mol) in acetonitrile (50 cm^3). The suspension was refluxed at 80–90 °C for 16 h. Solvent was then removed *in vacuo* to give a yellow oil. Purification by flash chromatography [diethyl ether-hexane (1:1, v/v)] gave mixture of **5** and **6** (6.8 g, 93%) as a colorless oil. Pure **5** and **6** was obtained by repeated flash chromatography [diethyl ether-hexane (1 : 1 v/v)]. The more polar *ester* **5** was obtained as colorless needles, m.p. 58—60 °C (lit.,[8] m.p. 60 °C); R_f 0.31 [diethyl ether-hexane (1 : 1 v/v)]; $[\alpha]_D^{24}$ – 5.4 (*c* 1.1 in $CHCl_3$) {lit.,[8] $[\alpha]_D^{22}$ – 3.9 (*c* 1.1 in $CHCl_3$)}; ν_{max}/cm^{-1} 1740 (C=O saturated ester); δ_H ($CDCl_3$) 1.34 (3 H, s, Me), 1.37 (3 H, s, Me), 1.44 (3 H, s, Me), 1.50 (3 H, s, Me), 2.47 (1 H, dd, *J* 7.2 and 15.3, 2-H_b), 2.55 (1 H, dd, *J* 7.7 and 15.3, 2-H_a), 3.71 (3 H, s, $CO_2\underline{Me}$), 3.79 (1 H, dd, *J* 3.7 and 7.6, 6-H), 3.99 (1 H, dd, *J* 4.5 and 8.7, 8-H_b), 4.08 (1 H, dd, *J* 6.2 and 8.7, 8-H_a), 4.38 (1 H, ddd, *J* 4.5, 6.2 and 7.6, 7-H), 4.48 (1 H, t, *J* 7.4, 3-H), 4.64 (1 H, d, *J* 6.1, 4-H), 4.81 (1 H, dd, *J* 3.7 and 6.1, 5-H); *m/z* (EI) 59 (19.68%, CO_2Me^+), 101 (65.72, $C_5O_2H_9^+$), 243 (14.71, $M^+ - CH_2CO_2Me$), 301 (12.84, $M^+ - Me$).

The less polar *ester* **6** was obtained as a colorless oil, R_f 0.36 [diethyl ether-hexane (1 : 1 v/v)]; $[\alpha]_D^{24}$ – 6.2 (*c* 2.3 in $CHCl_3$) {lit.,[8] $[\alpha]_D^{22}$ – 5.9 (*c* 1.0 in $CHCl_3$)}; ν_{max}/cm^{-1} 1740 (C=O saturated ester); δ_H ($CDCl_3$) 1.33 (3 H, s, Me), 1.37 (3 H, s, Me), 1.44 (3 H, s, Me), 1.46 (3 H, s, Me), 2.72 (1 H, dd, *J* 6.5 and 16.8, 2-H_b), 2.81 (1 H, dd, *J* 7.2 and 16.8, 2-H_a), 3.71 (3 H, s, $CO_2\underline{Me}$), 3.90–3.97 (1 H, m, 3-H), 4.02 (1 H, dd, *J* 4.8 and 8.7, 8-H_b), 4.07 (1 H, dd, *J* 6.0 and 8.7, 8-H_a), 4.34–4.41 (1 H, m, 7-H), 4.76–4.77 (2 H, m, 4-H and 5-H); *m/z* (EI) 59 (25%, CO_2Me^+), 101 (88.52, $C_5O_2H_9^+$), 243 (2.38, $M^+ - CH_2CO_2Me$), 310 (39.65, $M^+ - Me$). The ratio of **5** : **6** (*ca.* 1 : 1) was determined by ^1H NMR.

Epimerization of 5 to 6 by sodium methoxide.[8]—Sodium methoxide (1.1 g, 0.021 mol) was added in one portion to a stirred solution of a mixture of **5** and **6** (6.6 g, 0.021 mol) in dry methanol (50 cm^3). The solution was stirred at room temperature for 48 h. The solution was then filtered through a bed of silica gel topped with Celite. Evaporation of solvent from the filtrate gave a pale yellow syrup. Purification by flash chromatography [diethyl ether-hexane (2 : 3 v/v)] gave a mixture of **5** and **6** (6.1 g, 93%) as a colorless oil. The ratio of **5** : **6** (*ca.* 2 : 5) (lit.,[8] **5** : **6** = 1 : 4) was determined by ^1H NMR.

Methyl 3,6-*anhydro*-2-*deoxy*-4,5-O-*isopropylidene*-D-glycero-D-galacto-*octanoate* 7.—A solution of the ester **6** (4.5 g, 0.014 mol) in acetic acid (25 cm^3) and water (25 cm^3) was stirred at room temperature for 48 h. The solvents were then removed *in vacuo* to give a pale yellow oil. Purification by flash chromatography (diethyl ether) then afforded the *diol* **7** (4.1 g, 92%) as a colorless oil, R_f 0.23 (diethyl ether); (Found: C, 51.7; H, 7.4. $C_{12}H_{20}O_7$ requires C, 52.2; H, 7.3%); $[\alpha]_D^{24}$ – 7.2 (*c* 1.1 in $CHCl_3$); ν_{max}/cm^{-1} 1738 (C=O saturated ester) and 3445 (OH); δ_H ($CDCl_3$) 1.34 (3 H, s, Me), 1.48 (3 H, s, Me), 2.74 (1 H, dd, *J* 6.7 and 16.9, 2-H_b), 2.82 (1 H, dd, *J* 6.9 and 16.9, 2-H_a), 3.55 (1 H, dd, *J* 3.4 and 7.9, 6-H), 3.67–3.74 (4 H, m, $CO_2\underline{Me}$ and 8-H_b with $CO_2\underline{Me}$ as a singlet at 3.71 ppm), 3.82 (1 H, dd, *J* 3.5 and 6.9, 3-H), 3.93 (1 H,

dd, *J* 3.5 and 6.9, 3-H), 3.91–3.96 (1 H, m, 7-H), 4.76 (1 H, dd, *J* 3.5 and 6.1, 4-H), 4.84 (1 H, dd, *J* 3.7 and 6.1, 5-H); *m/z* (EI) 123 (36.69%, $M^+ - C_2H_5O_2 - C_3H_6O_2 - H_2O$), 141 (14.97, $M^+ - C_2H_5O_2 - C_3H_6O_2$), 169 (6.92, $MH^+ - CO_2Me - CH_3O - H_2O$), 187 (32.75, $MH^+ - CO_2Me - CH_3O$), 261 (9.47, $M^+ -$ Me).

***Aldehyde* 8**.—Sodium metaperiodate (693 mg, 3.24 mmol) was added in one portion to a stirred solution of the diol **7** (596 mg, 2.16 mmol) in methanol (20 cm^3) and water (1 cm^3) at room temperature. After being stirred at room temperature for 15 min, the mixture was diluted with chloroform (50 cm^3) and filtered through a bed of silica gel topped with Celite. The filtrate was then concentrated *in vacuo* to give the *aldehyde* **8**. The aldehyde was then dried by concentration with toluene several times *in vacuo*. The aldehyde was used in the next step without further purification.

***Methyl* 3,6-*anhydro*-2-*deoxy*-4,5-O-*isopropylidene*-7-C-*phenyl*-D-glycero-D-galacto-*heptanoate* 9 and *Methyl* 3,6-*anhydro*-2-*deoxy*-4,5-O-*isopropylidene*-7-C-*phenyl*-L-glycero-D-galacto-*heptanoate* 10**.—The aldehyde **8** prepared from the previous experiment was dissolved in THF (20 cm^3) and the solution was cooled at 0 °C. Phenylmagnesium bromide in THF (2.2 cm^3, 1.0 dm mol^{-1}) was then added at 0 °C and the mixture was then stirred at 0 °C for a further 2 h. The mixture was quenched with saturated ammonium chloride (10 cm^3) and was diluted with dichloromethane (20 cm^3). The mixture was extracted with dichloromethane (2 × 20 cm^3). The combined organics were then dried ($MgSO_4$) and filtered. Solvent removal *in vacuo* gave a pale yellow oil. Flash chromatogaphy [diethyl ether-hexane (3 : 2 v/v)] gave an inseparable mixture of **9** and **10** (362 mg, 52% from diol **3**) as colorless oils. The ratio of **9** : **10** (*ca.* 1 : 1) was determined by ^1H NMR spectral analysis.

3,6-*Anhydro*-2-*deoxy*-7-C-*phenyl*-D-glyceo-D-galacto-*heptono*-1,4-*lactone* 1 and 3,6-*anhydro*-2-*deoxy*-7-C-*phenyl*-L-glyceo-D-galacto-*heptono*-1,4-*lactone* 2.—A solution of the alcohols **9** and **10** (362 mg, 1.12 mmol) in acetic acid (16 cm^3) and water (4 cm^3) was stirred at 80–90 °C for 19 h. The solvents were then removed *in vacuo* to give a pale yellow oil. Purification by flash chromatography (diethyl ether) then afforded the *lactones* **1** and **2** (225 mg, 80%) as colorless oils. Lactones **1** and **2** was separated by flash chromatography [chloroform-methanol (97 : 3 v/v)] using aluminum oxide (Grade III, acidic) as the stationary phase. The more polar *lactone* **1** was obtained as colorless needles, m.p. 155—156 °C; R_f 0.27 (diethyl ether), 0.23 {[chloroform-methanol (97 : 3 v/v)] on neutral alumina}; (Found: C, 62.3; H, 5.4. $C_{13}H_{14}O_5$ requires C, 62.4; H, 5.6%); $[\alpha]_D^{24}$ – 24 (*c* 0.5 in $CHCl_3$); ν_{max}/cm^{-1} 1775 (C=O) and 3410 (OH); δ_H (D_2O with HOD at 4.80 ppm) 2.55 (1 H, dd, *J* 2.4 and 19.1, 2-H_a), 2.88 (1 H, dd, *J* 7.7 and 19.1, 2-H_b), 4.07 (1 H, dd, *J* 3.7 and 9.3), 4.60 (1 H, m, 3-H), 4.66 (1 H, dd, *J* 3.7 and 5.3, 5-H), 4.87 (1 H, d, *J* 9.3, 7-H), 5.23 (1 H, t, *J* 6.1, 4-H); δ_H ($CDCl_3 + D_2O$) 2.76–2.78 (2 H, 2 × s, 2-H_a and 2-H_b), 3.93 (1 H, dd, *J* 4.1 and 7.4, 5-H), 4.56 (1 H, dd, *J* 4.1 and 5.2, 6-H), 4.64 (1 H, dt, *J* 5.0 and 6.1, 3-H), 4.96–5.02 (2 H, m, 4-H and 7-H), 7.32–7.44 (5 H, m, Ph); δ_C (acetone-d_6) 36.48, 71.70, 72.43, 76.55, 83.32, 85.43, 127.54, 127.73, 128.37, 143.30, 175.94; *m/z* (EI) 232 (11.03%, $M^+ - H_2O$).

The less polar *lactone* **2** was also obtained as colorless needles, m.p. 124—125 °C; R_f 0.27 (diethyl ether), 0.36 {[chloroform-methanol (97 : 3 v/v)] on neutral alumina}; (Found: C, 62.1; H, 5.6. $C_{13}H_{14}O_5$ requires C, 62.4; H, 5.6%); $[\alpha]_D^{28}$ + 13 (*c* 0.3 in $CHCl_3$); ν_{max}/cm^{-1} 1773 (C=O) and 3412 (OH); δ_H ($CDCl_3 + D_2O$) 2.60 (1 H, dd, *J* 6.7 and 18.8, 2-Hb), 2.69 (1 H, dd, *J* 3.8 and 18.8, 2-Hb), 3.83 (1 H, t, *J* 4.8, 5-H), 4.06 (1 H, t, *J* 4.8, 6-H), 4.53 (1 H, dt, *J* 3.8 and 6.6, 3-H), 4.78 (1 H, t, *J* 6.3, 4-H), 4.91 (1 H, d, *J* 5.2, 7-H), 7.13–7.33 (5 H, m, Ph); δ_C ($CDCl_3$) 35.95, 71.18, 71.53, 75.72, 82.58, 85.42, 126.63, 127.64, 128.10, 140.26, 176.23; *m/z* (EI) 232 (5.89%, $M^+ - H_2O$).

3,6-*Anhydro*-2-*deoxy*-D-glycero-D-galacto-*octono*-1,4-*lactone* 11.—A solution of the ester **6** (3.3 g, 0.011 mol) in methanol (25 cm^3) was stirred at room temperature. Trifluoroacetic acid (15 cm^3) and water (15 cm^3) were added and the solution was stirred at reflux 70–80 °C for 24 h. Solvents were removed *in vacuo* to give a white solid (1.7 g, 81%). Purification by recrystallization from hot ethanol gave the *triol* **11** as colorless plates, m.p. 169—171 °C; R_f 0.33 [methanol-chloroform (1 : 4 v/v)]; (Found: C, 46.8; H, 6.0. $C_8H_{12}O_6$ requires C, 47.1; H, 5.9%); $[\alpha]_D^{24}$ – 63 (*c* 2.0 in H_2O); ν_{max}/cm^{-1} 1793 (γ-lactone) and 3355 (OH); δ_H ($CDCl_3$) 2.66 (1 H, dd, *J* 2.5 and 19.2, 2-H_b), 2.97 (1 H, dd, *J* 7.7 and 19.2, 2-H_a), 3.61 (1 H, dd, *J* 5.7 and 12.1, 8-H_b), 3.76 (1 H, dd, *J* 2.8 and 12.1, 8-H_a), 3.78 (1 H, dd, *J* 3.5 and 8.7, 6-H), 3.94 (1 H, ddd, *J*

2.8, 5.7 and 8.7, 7-H), 4.55 (1 H, dd, *J* 3.5 and 5.6, 5-H), 4.74 (1 H, ddd, *J* 2.5, 5.6 and 7.7, 3-H), 5.20 (1 H, dd, *J* 5.6 and 6.5 4-H); *m/z* (EI) 126 (64.13%, $MH^+ - C_2O_2H_5 - H_2O$), 187 (5.98, $MH^+ - H_2O$), 205 (4.82, MH^+).

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