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SYNTHESIS AND CHARACTERIZATION OF METHYL 6-*O*-α- AND -β-D-GALACTOPYRANOSYL-β-D-GALACTOPYRANOSIDE

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ABSTRACT

Sequential tritylation, acetylation and detritylation of methyl β-D-galactopyranoside gave crystalline methyl 2,3,4-tri-*O*-acetyl-β-D-galactopyranoside (**4**) and methyl 2,3,6-tri-*O*-acetyl-β-D-galactopyranoside, the latter being the minor product resulting from acetyl migration. Reaction of **4** with 2,3,4,6-tetra-*O*-acetyl-α-D-galactosyl bromide in benzene, in the presence of mercuric cyanide and mercuric bromide, gave the α- and β-D-(1→6)-linked disaccharides (**7** and **9**, respectively) in high yield, and their structure was confirmed by ^{1}H- and ^{13}C-n.m.r. 1d. and 2d. spectroscopy. *O*-Deacetylation of **7** gave the hitherto unknown, crystalline methyl 6-*O*-α-D-galactopyranosyl-β-D-galactopyranoside. *O*-Deacetylation of **9** gave the corresponding, β-D-linked disaccharide methyl glycoside, the physical constants of which are discussed with respect to controversial data in the literature.

INTRODUCTION

Methyl β-glycosides of (1→6)-β-D-galacto-oligosaccharides are important ligands in studies of binding constants of immunoglobulins having anti (1→6)-β-D-galactan specificity. To date, only a limited number of compounds of this type has been chemically synthesized and studied from the aforementioned point of view. A continuation of our systematic studies in this field[1–4] required efficient methods for the synthesis of these compounds. A systematic, chemical synthesis of methyl β-glycosides of (1→6)-β-D-galacto-oligosaccharides had previously been undertaken, and the di- and tri-saccharide in this series were prepared by Srivastava *et al.*[5]. Their reaction scheme offers the possibility for a stepwise extension of galacto-oligosaccharides having the (1→6) linkage, but the preparation of the monomers involves the not readily accessible 1,6-anhydro-3,4-*O*-isopropylidene-β-D-galactopyranose, necessary for the desired, enhanced β-stereoselectivity of the glycosylation reaction. More recently, Gorin[6] reported the synthesis of isomeric methyl *O*-D-galactopyranosyl-β-D-galactopyranosides, among them methyl 6-*O*-α- and -β-D-galactopyranosyl-β-D-galactopyranosides, the title compounds. The α anomer was obtained in admixture with the β anomer, and, therefore, the compound was not characterized by physical constants.

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In the past, this laboratory developed a method for the stepwise preparation of β-D-(1→6)-linked D-galacto-oligosaccharides by the use of a chloroacetyl group as a temporary blocking group for O-6 in D-galactopyranose[7]. We are in the process of preparing the corresponding methyl β-glycosides of these oligosaccharides, and to prepare **9** we decided to use 2,3,4,6-tetra-*O*-acetyl-α-D-galactosyl bromide as the glycosylating agent, and any readily available 2,3,4-tri-*O*-substituted methyl β-D-galactopyranoside as the initial nucleophile. Our choice for the latter was methyl 2,3,4-tri-*O*-acetyl-β-D-galactopyranoside. We have found only one reference in the literature where this simple compound was described; Mackie and Perlin[8] obtained it as an amorphous substance, and it was not properly characterized. Therefore, we decided to re-examine the preparation of methyl 2,3,4-tri-*O*-acetyl-β-galactopyranoside, a compound we consider to be a generally useful intermediate.

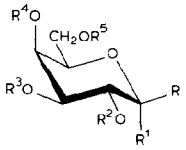
Before undertaking the sequential synthesis of methyl β-D-glycosides of (1→6)-β-D-galacto-oligosaccharides, there was one more problem that had to be addressed. Two sets of physical constants are available in the literature as characterizing the first member of the series of these compounds, namely, methyl 6-*O*-β-D-galactopyranosyl-β-D-galactopyranoside. The difference in the m.p. reported, 160–165° (dec.[5]) *vs.* 220–221° (ref. 6), might have been due to dimorphism of the compound, although a different thermal stability of two allotropic modifications would be rather unusual. More surprising, however, are the quite different values, and the opposite sign, of the reported optical rotations, +18.7 (ref. 5) *vs.* −9° (ref. 6). We now report the synthesis of compound **10** *via* an independent route, to verify the structure by spectral analysis, and to provide the correct physical constants.

RESULTS AND DISCUSSION

Methyl 6-*O*-trityl-β-D-galactopyranoside and its 2,3,4-triacetate were first prepared at a time when chromatography and other modern analytical methods were not available. It should not, therefore, be surprising that our preparation of **2**, isolated by chromatography, and of compound **3**, obtained from it, showed melting points higher than those reported[9]. During detritylation of **2**, either with hydrobromic acid in acetic acid or with dilute acetic acid alone, the formation of side products was observed. The presence of by-products in the resulting, crude product probably prevented the isolation of **5** in the pure state in the earlier[8] work. One of the by-products, not studied here, was presumably the tetraacetate of **1**. It co-chromatographed with methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside, and acetylation of HO-6 of hexopyranosides during concentration of their solutions in the presence of acetic acid had previously been observed (*cf.*, ref. 1).

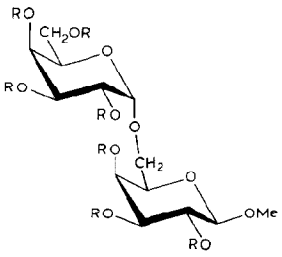
When the product of the detritylation of **2** was chromatographed, another by-product, moving only slightly faster in t.l.c. than the major product, was isolated in crystalline form. By analyses of its ^{13}C- and ^{1}H-n.m.r. spectra, it was found to have resulted from acetyl-group migration, the compound being methyl 2,3,6-tri-*O*-acetyl-β-D-galactopyranoside (**5**). The major product of detritylation of **2** was

the desired 2,3,4-tri-*O*-acetyl derivative **4**. In our hands, the compound crystallized readily, and its n.m.r.-spectral data were consistent with the structure expected. The observed ^{13}C- and ^{1}H-n.m.r. chemical-shifts and first-order coupling-constants are given in the Experimental section, and only the following, salient points are noted here. Consistent with the downfield shift of the signal of the proton that is part of an HCOCOR group, the signal of H-4 in the spectrum of **4** appeared at δ 5.40, and that of the geminal protons of the CH_2OH group was shifted upfield to δ 3.85. On the other hand, the ^{1}H-n.m.r. spectrum of **5** showed the signal of H-4 upfield, at δ 4.07, H-4 being coupled to the proton of HO-4. The signal of the methylene protons of the CH_2OCOMe group appears in the spectrum of **5** as a two-proton doublet downfield, at δ 4.33. The ^{13}C-n.m.r. spectra of **4** and **5** were readily interpreted by using as an aid the unambiguously assigned[10] spectra of methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside and benzyl 2,3,6-tri-*O*-acetyl-β-D-galactopyranoside. The assignments were then confirmed by 2d. chemical-shift, ^{13}C–^{1}H- correlation experiments.

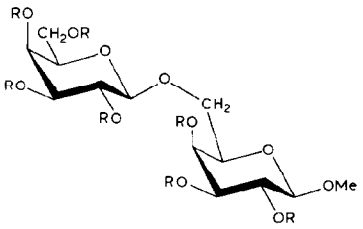


	R	R^1	R^2	R^3	R^4	R^5
1	OMe	H	H	H	H	H
2	OMe	H	Ac	Ac	Ac	Tr
3	OMe	H	H	H	H	Tr
4	OMe	H	Ac	Ac	Ac	H
5	OMe	H	Ac	Ac	H	Ac
6	H	Br	Ac	Ac	Ac	Ac

Tr = Ph_3C



7 R = Ac
8 R = H



9 R = Ac
10 R = H
11 R = Bz

Condensation of **4** with 2,3,4,6-tetra-*O*-acetyl-α-D-galactosyl bromide (**6**) in benzene, in the presence of mercuric cyanide and mercuric bromide, gave the α- and β-D-linked disaccharides **7** and **9**, in the ratio of ~1:10. The disaccharides were isolated by column chromatography in very good, combined yield. The stereochemistry of the inter-sugar linkage in **7** and **9**, tentatively assigned on the basis of specific optical rotation, was confirmed by ^{1}H- and ^{13}C-n.m.r. spectroscopy. This is in contrast to the report of the previous synthesis[5] of **10**, where the coincidence of the anomeric signals with benzylic- and other ring-protons prevented the identification by ^{1}H-n.m.r. spectroscopy of the configuration of the D-galactosyl linkages in the products of the coupling reaction. The spectra of peracetates **7** and **9** were evaluated by first-order analysis (see the Experimental section). Signals for H-1 in the spectra of **7** and **9** appear as doublets at δ 4.43 and 4.41, respectively, and both show a $J_{1,2}$ value of 8 Hz (*c.f.*, δ 4.44 and $J_{1,2}$ 8 Hz found in the spectrum of **4**). Diagnostically significant doublets of H-1′ are shifted downfield, and show $J_{1',2'}$ 3.5 and 8 Hz, consistent with **7** and **9** respectively containing α and β inter-sugar linkages. The same could be concluded from the data extracted from the ^{13}C-n.m.r. spectra of **7** and **9**, which were tentatively interpreted by using, as aids, unambiguously assigned spectra of **4** and methyl 2,3,4,6-tetra-*O*-acetyl-α- and -β-D-galactopyranoside[10,11]. Substitution shift-effects due to glycosylation were also taken into account. Thus, lines of anomeric carbon atoms, appearing at δ 102.2 and 96.6 in the spectrum of **7**, and δ 102.0 and 100.7 in that of **9**, identified the stereochemistry at the anomeric center. As a result of glycosyloxylation at C-6 of the D-galactoside residue, the signals of C-6 in the spectra of **7** and **9** would be expected to appear downfield, compared to the chemical shift of C-6 for **4**. The lines corresponding to the glycosyloxylated C-6 atoms in the spectra of **7** and **9** were identified, by off-resonance-decoupling experiments, as those appearing at δ 65.7 and 66.8, respectively (*c.f.*, δ 60.2 for C-6 in the spectrum of **4**). It may be mentioned that the stronger downfield, α-shift effect of β-glycosyloxylation, as compared to that of α-glycosyloxylation, found here (6.6 *vs.* 5.5 p.p.m.) is consistent with shift effects found in the spectra of other pairs of α- and β-linked oligosaccharides[12–14]. On the other hand, the upfield β-effect due to glycosyloxylation was found to be stronger for α-D-galactosyloxylation than for β-D-galactosyloxylation (δ 71.5 and 72.2 for C-5 in the spectrum of **7** and **9**, respectively; *c.f.*, δ 73.2 for C-5 in the spectrum of **4**).

In agreement with the expected similarity of the chemical shift for carbon atoms that occupy the same position relative to the glycosidic linkage[15], C-3,C-3′ and C-2,C-2′ appear in the spectrum of **9** as sets of two lines showing similar chemical shifts. Compound **7** constitutes a completely different situation. Here, C-2 and C-3 occupy the same position relative to a glycosidic linkage, but one (intersaccharidic) is α, whereas the other is β. Consequently, the signals of C-2′/C-2 appear much farther apart in the spectrum of **7** than that of **9**. This also holds for the C-3′/C-3 signals. The ^{13}C-line assignments made in the aforementioned way were confirmed by 2d., ^{13}C–^{1}H chemical-shift-correlation experiments. Also, the latter

technique allowed the selection of the correct lines for C-5′ in the spectrum of **9**, and for C-5, C-3, and C-3′ in that of **7**.

O-Deacetylation of **7** with sodium methoxide in methanol yielded the hitherto-unknown, crystalline methyl β-glycoside (**8**) of (1→6)-α-D-galactobiose. Methyl 6-*O*-β-D-galactopyranosyl-β-D-galactopyranoside (**10**) was obtained in the same way by *O*-deacetylation of **9**. Unlike the case of **10**, complete assignment of lines in the ^{13}C-n.m.r. spectrum of **8** was not possible by comparison of the observed ^{13}C-n.m.r. data with those found[11] for methyl α- and β-D-galactopyranoside. Assignments given in the Experimental section were made by the differential-isotope-shift technique[16].

During the determination of the melting point of **10**, no sign of decomposition was observed [*c.f.* ref. 5, m.p. 160–165° (dec.)], and the m.p. and $[\alpha]_D$ found here for the compound compare well with the physical constants found for the same compound by Gorin[6]. Although this strongly suggested that the compound reported as having[5] the foregoing m.p., and $[\alpha]_D$ +18.7°, was not methyl 6-*O*-β-D-galactopyranosyl-β-D-galactopyranoside, the ^{13}C-n.m.r. chemical-shifts found in the spectrum of the compound by the previous authors[5] are virtually the same as those found here (the differences in the chemical shifts are so small that they may be presumed to arise from different conditions of the measurements). Undoubtedly, Srivastava *et al.*[5] had in hand the compound claimed, but we are unable to explain the striking differences between the physical constants reported here and by Gorin[6] and those given by Srivastava *et al.*[5].

EXPERIMENTAL

General. — Melting points were determined with a Büchi melting-point apparatus. Optical rotations were measured at 25° with a Perkin–Elmer automatic polarimeter, Model 241 MC. Preparative chromatography was performed by gradient elution from columns of slurry-packed Silica Gel 60 (Merck Cat. No. 9385). Thin-layer chromatography (t.l.c.) on glass slides coated with silica gel G (Analtech) was performed with *A*, 15:1 dichloromethane–methanol; *B*, 10:1 carbon tetrachloride–acetone; and *C*, 7:2 toluene–acetone. Detection was effected by charring with 5% sulfuric acid in ethanol.

Chemical ionization (c.i.) mass spectra were recorded with a Micromass 7070 F spectrometer. ^{13}C-N.m.r. spectra were recorded for solutions in D_2O (compounds **8** and **10**; internal standard MeOH, δ MeOH *vs.* Me_4Si, 49.0 p.p.m.) and $CDCl_3$ (internal standard Me_4Si) with a Varian FX 100 spectrometer, operated at 25.16 MHz. Proton and carbon 1d. and 2d. spectra were also recorded with a Nicolet 360 wide-bore, n.m.r. system, equipped with a Nicolet 1180 data system and a Model 293B pulse programmer. Protons were observed at 361.044 MHz, using an 8-μs pulse-width (8 μs = 90°) with a 5-s pulse repetition-time. A sweep width of ±1.500 kHz with quadrature detection, 32 k data points, and exponential broadening of 0.1 Hz were routinely applied. Carbon 1d. spectra were observed at

90.79 MHz, using a 25-μs pulse-width (25 μs = 90°), 16 k data points, and 5-s pulse repetition-rates. The sweep width of ±10.000 kHz with quadrature detection, and exponential multiplication of the free-induction decays gave theoretical broadening of 1.5 Hz. Simultaneous noise-decoupling was applied at the proton frequency. The 2d. carbon–proton correlation spectroscopy[18,19] was conducted with 128 different mixing times and 1 k data points. Sweep widths were restricted to the chemical-shift regions of main interest. COSY[20,21] experiments were performed by using 512 mixing times and 512 data points.

The almost colorless solution of hydrogen bromide in acetic acid that was used to prepare[17] bromide **6** was purchased from Fluka, A.G. Solutions in organic solvents were dried with anhydrous sodium sulfate, and evaporated at 40°/2 kPa.

*Methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-*D*-galactopyranoside* (**2**). — Trityl chloride (79 g, 283 mmol) was added in portions during 30 min to a stirred solution of **1** (50 g, 257 mmol) in dry pyridine (250 mL). Stirring was continued for 2 h at room temperature and for 3 h at 50°. T.l.c. (solvent *A*) then showed that the reaction was almost complete. Acetic anhydride (100 mL) was added portionwise during 1 h, and the mixture was kept overnight at room temperature. T.l.c. (solvent *B*) then showed that the reaction was complete and that, in addition to the desired product **2** (R_F 0.7), a minor product that did not contain a trityl group, presumably the tetra-acetate of **1** resulting from incomplete tritylation of **1**, was also present. Methanol (100 mL) was added in portions, with occasional cooling and, after 1 h at room temperature, the mixture was concentrated to half its volume, and poured into a vigorously stirred solution of sodium hydrogencarbonate containing ice. The solid product precipitated was collected by filtration, washed several times with water, and dissolved in dichloromethane. The solution was washed with water, dried, and evaporated, and the residue was chromatographed on a column of silica gel (750 g) with carbon tetrachloride → 20:1 carbon tetrachloride–acetone, to remove most of the impurities. Crystallization from ethanol gave several crops of **2** (total yield 113 g, 77.9%) which were chromatographically homogeneous. Recrystallization of a portion from the same solvent afforded material having m.p. 143–145° and $[\alpha]_D$ −52.7°(*c* 1.6, chloroform) {lit.[9] m.p. 138°, $[\alpha]_D$ −50.3°}; ^{13}C-n.m.r. data: δ 101.7 (C-1), 71.7 (C-5), 70.9 (C-3), 68.8 (C-2), 67.0 (C-4), 60.5 (C-6), and 56.6 (OMe).

Anal. Calc. for $C_{32}H_{34}O_9$: C, 68.31; H, 6.09. Found: C, 68.57; H, 6.21.

*Methyl 6-*O*-trityl-β-*D*-galactopyranoside* (**3**). — M Methanolic sodium methoxide (1 mL) was added to a suspension of **2** (2 g) in methanol (25 mL), and the mixture was stirred at room temperature with exclusion of atmospheric moisture. A clear solution formed after 15 min, and, after a total of 3 h, t.l.c. (solvent *C*) showed that the reaction was complete and that one product (R_F 0.1; *c.f.*, 0.7 for the starting material) was formed. The base was neutralized with Amberlite IR-120 (H^+) resin, whereupon the product crystallized. Dichloromethane was added to dissolve the crystals, the resin was filtered off, and the filtrate was concentrated to a small volume. The crystals that formed were collected, to give **3** in almost theoretical yield. Recrystallization of a portion gave material having m.p. 184–185°

and $[\alpha]_D$ −38° (*c* 1.1, chloroform) {lit.[9] m.p. 167–168° (sint. at 80°); $[\alpha]_D$ −39.5°}; ^{13}C-n.m.r. data: δ 103.9 (C-1), 73.7-double intensity (C-3, C-5), 71.7 (C-2), 69.1 (C-4), 62.7 (C-6), and 56.7 (OMe).

Anal. Calc. for $C_{26}H_{28}O_6$: C, 71.54; H, 6.46. Found: C, 71.34; H, 6.55.

Methyl 2,3,4- (**4**) *and 2,3,6-tri-*O*-acetyl-β-*D*-galactopyranoside* (**5**). — To a solution of the trityl derivative **2** (47 g) in acetic acid (250 mL), cooled to 0°, was added hydrogen bromide in acetic acid (25 mL), and the mixture was stirred for 1 min, and filtered onto a mixture of ice and water (1 L); the solid formed was collected by filtration, washed with ice water (thrice), and the filtrate, combined with the washings, thoroughly extracted with dichloromethane. The extract was backwashed with water, concentrated, and co-distilled with toluene to remove acetic acid. T.l.c. of the residue revealed three charring products (R_F 0.6, 0.35, and 0.3), the fastest moving of which (~5%) co-chromatographed with methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside. The crude product was resolved by chromatography on a column of silica gel to give, first, compound **5** (3.1 g, 11.5%); m.p. 108–109° (from ether containing a little dichloromethane, twice), $[\alpha]_D$ +1° (*c* 1.2, chloroform); ^{13}C-n.m.r. data: δ 101.9 (C-1), 73.4 (C-3), 72.2 (C-5), 69.2 (C-3), 67.0 (C-4), 62.7 (C-6), and 56.6 (OMe); ^{1}H-n.m.r. data: δ 4.40 (d, H-1), 5.25 (dd, H-2), 4.94 (dd, H-3), 4.07 (dd, H-4), 3.76 (t, H-5), 4.33 (d, H-6,6′), and 3.05 (d, OH, disappears on deuteration), $J_{1,2}$ 7.9, $J_{2,3}$ 10.1, $J_{3,4}$ 3.3, $J_{4,5}$ not observed, $J_{5,6}$ 6.2, $J_{6,6'}$ not observed, and $J_{4,OH}$ 5.5 Hz.

Anal. Calc. for $C_{13}H_{20}O_9$: C, 48.74; H, 6.29. Found: C, 48.96; H, 6.58.

Subsequently eluted was compound **4** (13 g, 48.4%); m.p. 125–126° (from dichloromethane–isopropyl ether, twice), $[\alpha]_D$ +5.2° (*c* 1.1, chloroform). {lit.[8] $[\alpha]_D$ −9.8° for amorphous **4**}; ^{13}C-n.m.r. data: δ 101.8 (C-1), 73.2 (C-5), 70.9 (C-3), 68.9 (C-2), 67.5 (C-4), 60.2 (C-6), and 56.7 (OMe); ^{1}H-n.m.r. data: δ 4.44 (d, H-1), 5.21 (dd, H-2), 5.06 (dd, H-3), 5.40 (d, H-4), 3.85–3.55 (m, H-5,6,6′), 2.75 (br. s, OH), $J_{1,2}$ 8, $J_{2,3}$ 10.5, and $J_{3,4}$ 3.2 Hz.

Anal. Calc. for $C_{13}H_{20}O_9$: C, 48.74; H, 6.29. Found: C, 48.45; H, 6.15.

*Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,4-tri-*O*-acetyl-α-* (**7**) *and -β-*D*-galactopyranosyl)-β-*D*-galactopyranoside* (**9**). — The glycosyl bromide **6** (1.86 g, 4.5 mmol) was added to a mixture of the nucleophile **4** (0.96 g, 3 mmol), mercuric cyanide (0.57 g, 2.25 mmol), mercuric bromide (0.25 g), and Drierite (3 g) in dry benzene (5 mL) that had been stirred for 2 h. The suspension, protected from atmospheric moisture, was stirred for 16 h at room temperature, when t.l.c. (solvent *C*) showed the presence of one major (R_F 0.50) and two minor products (R_F 0.55 and 0.7), together with traces of unreacted **4** (R_F 0.4), and the product of hydrolysis of **6** (R_F 0.45). The mixture was filtered, the solids were washed several times with dichloromethane, and the filtrate and washings were combined, washed with aqueous potassium bromide solution, to remove the mercuric salts, dried, evaporated, and the residue chromatographed, to give **7** (R_F 0.55; 0.15 g, 7.7%). Two recrystallizations from ethanol gave material having m.p. 165–165.5° and $[\alpha]_D$ +86° (*c* 0.94, chloroform); ^{13}C-n.m.r. data: δ 102.2 (C-1), 96.6 (C-1′), 71.5 (C-5), 71.2 (C-3),

68.9 (C-2), 67.9 (C-3'), 67.6, 67.4 double intensity (C-2',4,4'), 66.6 (C-5'), 65.7 (C-6), 61.6 (C-6'), and 57.0 (OMe); ^{1}H-n.m.r. data: δ 4.43 (d, H-1), 4.96 (d, H-1'), 5.19 (dd, H-2), 5.12 (dd, H-2'), 5.02 (dd, H-3), 5.31 (dd, H-3'), 5.44 (dd, H-4,4'), 3.88 (m, H-5), 4.24 (m, H-5'), 3.81–3.47 (m, H-6,6'), 4.17–4.03 (m, H-6',6'), and 3.53 (s, OMe), $J_{1,2}$ 8, $J_{1',2'}$ 3.5 Hz.

Anal. Calc. for $C_{27}H_{38}O_{18}$: C, 49.84; H, 5.88. Found: C, 50.20; H, 5.73.

Material having R_F 0.5 was obtained as colorless, foamy **9** (1.49 g, 76.5%) which showed $[\alpha]_D$ −13.5° (*c* 1.2, chloroform); ^{13}C-n.m.r. data: δ 102.0 (C-1), 100.7 (C-1'), 72.2 (C-5), 71.1, 70.9 (C-3,3'), 70.8 (C-5'), 68.9, 68.6 (C-2,2'), 67.7 (C-4), 67.1 (C-4'), 66.8 (C-6), 61.3 (C-6'), 56.9 (OMe); ^{1}H-n.m.r. data: δ 4.41 (d, H-1), 4.58 (d, H-1'), 5.18 (m, H-2,2'), 5.01 (m, H-3,3'), 5.38 (t, H-4,4'), 3.98–3.72 (m, H-5,5',6,6'), 4.15 (m, H-6'6'), 3.55 (s, OMe), $J_{1,2}$ 8, $J_{1',2'}$ 8 Hz.

Anal. Calc. for $C_{27}H_{38}O_{18}$: C, 49.84; H, 5.88. Found: C, 49.88; H, 6.07.

An intermediate, mixed fraction (0.08 g) was also obtained. Both compounds showed a peak at *m/z* 668 (M + 18) in their NH_3-c.i.-mass spectrum.

Methyl 6-O-α- (**8**) *and -β-*D*-galactopyranosyl-β-*D*-galactopyranoside* (**10**). — A solution of **7** (80 mg) in methanol (5 mL) was treated with M sodium methoxide in methanol (1 mL) for 24 h. The solution was made neutral with Amberlite IR-120 (H^+) resin and evaporated, to give **8** in almost theoretical yield. Recrystallization from methanol (twice) gave material of m.p. 161–162°, $[\alpha]_D$ +107° (*c* 1, water); ^{13}C-n.m.r. data: δ 103.9 (C-1), 98.4 (C-1'), 73.0 (C-5), 72.9 (C-3), 71.1 (C-5'), 70.8 (C-2), 69.6 (C-3'), 69.4 (C-4'), 68.8 (C-4), 68.3 (C-2'), 66.4 (C-6), 61.3 (C-6'), and 57.2 (OMe).

Anal. Calc for $C_{13}H_{24}O_{11}$: C, 43.81; H, 6.79. Found: C, 43.67; H, 6.58.

Compound **10**, obtained similarly from **9**, when recrystallized from methanol and dried for 3 h at 100°, had m.p. 218–219°, $[\alpha]_D$ −9.5° (*c* 1.25, water) {lit.[6] m.p. 220–221°, $[\alpha]_D$ −9° (*c* 0.5, water)}; ^{13}C-n.m.r. data: δ 104.0 (C-1), 103.4 (C-1'), 75.3 (C-5'), 73.9 (C-5), 72.8 double intensity (C-3,3'), 70.9, 70.8 (C-2,2'), 69.0 (C-6), 68.8 double intensity (C-4,4'), 61.1 (C-6'), and 57.4 (OMe).

Anal. Calc for $C_{13}H_{24}O_{11}$: C, 43.81; H, 6.79. Found: C, 43.53; H, 7.05.

The corresponding perbenzoate **11**, prepared by conventional benzoylation of **10**, had m.p. 253.5–254°, $[\alpha]_D$ +156.6° (*c* 1, chloroform); ^{13}C-n.m.r. data: δ 102.2 (C-1), 101.3 (C-1'), 73.2 (C-5), 71.7, 71.6 (C-3,3'), 71.3 (C-5'), 69.8 double intensity (C-2,2'), 68.7, 68.2, 68.0 (C-4,6,4'), 61.8 (C-6'), and 56.8 (OMe).

Anal. Calc. for $C_{62}H_{52}O_{18}$: C, 68.62; H, 4.83. Found: C, 68.56; H, 4.48.

Compounds **8** and **10** showed a peak at *m/z* 374 (M + 18) in their NH_3-c.i. mass spectra.

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