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Note

Unexpected formation of the 3,6-anhydro and 6-*O*-methyl-1-fluoro derivatives of galabiose on attempted substitution of HO-6 by fluorine in methyl 4-*O*-α-D-galactopyranosyl-β-D-galactopyranoside (methyl β-D-galabioside)

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During a study of the specific adhesion of micro-organisms and toxins to carbohydrates, we have prepared derivatives (*i.e.*, *O*-methyl, deoxy, *C*-alkyl, and deoxyfluoro) of methyl 4-*O*-α-D-galactopyranosyl-β-D-galactopyranoside (methyl β-D-galabioside)[1,2]. In continuation of the synthetic work, we wished to prepare methyl 6-deoxy-6-fluoro-β-D-galabioside by treatment of methyl 2,3-di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-β-D-galactopyranoside[2] (**1**) [or, alternatively, methyl 2,3-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-β-D-galactopyranoside[2] (**2**)] with diethylaminosulfur trifluoride (DAST) or trifluoromethanesulfonic anhydride and tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF), reagents that are commonly used to substitute hydroxyl groups in carbohydrates for fluorine without competing elimination[3]. However, treatment of **1** or **2** with these reagents gave minor amounts of the desired products, whereas the major products were formed by cyclisation, migration, or elimination. We now report on these unexpected reactions.

Treatment of **1**[2] with DAST in dichloromethane gave the 3,6-anhydropyranoside **3** (73%) but not the desired substitution product. Compound **3** displayed a complex ^{1}H-n.m.r. spectrum that did not permit a conclusive structural assignment. Hydrogenolysis of **3** and then acetylation gave the penta-acetate **4**. The resonances for H-4,5,6*endo* of the 3,6-anhydropyranosidic ring of **4** were not resolved, but the small values of $J_{1,2}$, $J_{2,3}$, $J_{3,4}$, and $J_{5,6exo}$ (Table I) were in good agreement with those calculated using the program 3JHH[4] (Table I). The ^{1}H-n.m.r. data also compared well with those reported for **5**[5] and **6**[6] (Table I).

The formation of **3** from **1** most likely occurred by nucleophilic attack of BzlO-3 on C-6 (activated by reaction of HO-6 with DAST) and formation of a benzyl cation. Similar displacement of sulfonates and iodide ion from C-6 of

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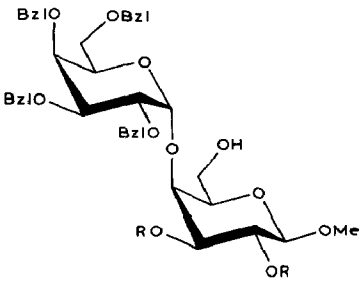
TABLE I

^{1}H-N.M.R. DATA OF THE 3,6-ANHYDROPYRANOSE RESIDUE FOR **4–6**

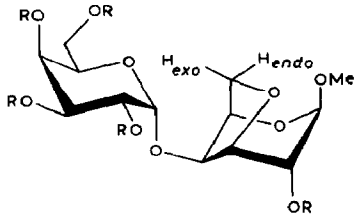
Atom	*Chemical shifts (δ, p.p.m.)*		
	4[a]	**5**[a,b]	**6**[a,c]
H-1	4.45	4.84[d]	5.28[d]
H-2	5.00	5.14	5.19
H-3	4.53	4.40	4.40
H-4	4.23–4.31	5.37[e]	5.41[e]
H-5	–"–	4.45	4.46
H-6*endo*	–"–	4.14	4.15
H-6*exo*	3.90	3.97	3.98

	Coupling constants (J, Hz)			
	4[a]	**5**[a,b]	**6**[a,c]	**4**[f]
1,2	<0.5	3.0[d]	2.7[d]	1.8
2,3	4.8	5.1	5.4	4.4
3,4	<0.5	<0.5	0	1.1
4,5	[g]	1.9	1.8	2.4
5,6*endo*	[g]	<0.5	0	1.3
5,6*exo*	2.9	2.8	2.9	3.4
6*endo*,6*exo*	9.8	10.5	10.4	[h]

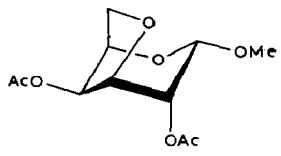
[a]$CDCl_3$ (internal Me_4Si). [b]Data from ref. 5. [c]Data from ref. 6. [d]Data not comparable due to different anomeric configuration. [e]Data not comparable due to 4-acetylation in **5** and **6**. [f]Calculated according to the Karplus equation for the minimum energy conformations of **4** (obtained from Allinger's MM2-82 program[7]) using the program 3JHH[4]. [g]Could not be determined due to overlap of the resonances for H-4, H-5, and H-6*endo*. [h]Cannot be calculated with 3JHH,



1 R = Bzl
2 R = Bz



3 R = Bzl
4 R = Ac



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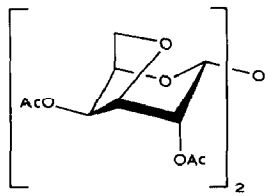
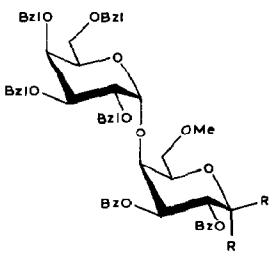


6

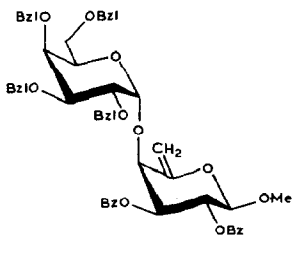
galactopyranosides occurs by intramolecular participation of 3-*O*-methyl[8], 3-*O*-benzyl[9], or 3-*O*-glycosyl[10] substituents. Furthermore, methyl 3,6-anhydro-β-D-galactopyranoside was formed on treatment of methyl β-D-galactopyranoside with tribromoimidazole, triphenylphosphine, and imidazole[11].

Attempts to prepare methyl 6-deoxy-β-D-galabioside from the 6-tosylate of **1** by reduction with lithium triethylborohydride or *via* substitution with sodium iodide gave **3** as the only product[2]. In summary, treatment of **1** having various leaving groups on C-6 with nucleophiles (F^-, H^-, and I^-), invariably gave the 3,6-anhydropyranoside **3**. Therefore, no attempts were made to prepare methyl 6-deoxy-6-fluoro-β-D-galabioside by treatment of **1** with trifluoromethanesulfonic anhydride and TASF.

Treatment of the 2,3-dibenzoate **2**, in which the nucleophilicity of O-3 is decreased, with DAST yielded neither cyclised nor substituted products but gave a mixture of the 6-*O*-methylated galabiosyl fluorides **7** and **8** (51 and 9.5%, respectively). The chemical shifts[12] of the ^{19}F resonances and the large $J_{H\text{-}1,F}$ and $J_{C\text{-}1,F}$ values are consistent with fluorine substitution at C-1, but not at C-6 (Table II). The configuration at the anomeric position was determined[13] from the $J_{H\text{-}1,H\text{-}2'}$ $J_{H\text{-}2,F'}$ and $J_{C\text{-}3,F}$ values (Table II). The n.O.e. (4–8%) observed for the MeO hydrogens of **7** and **8** on saturation of H-6,6 and the coupling between the MeO group and H-6,6 ($^3J_{C,H\text{-}6}$ 3.0 and 4.2 Hz for **7** and **8**, respectively) showed that the methyl group was located at position 6.



7 R = F, R′ = H
8 R = H, R′ = F



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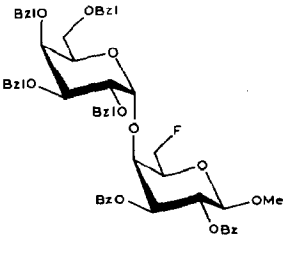
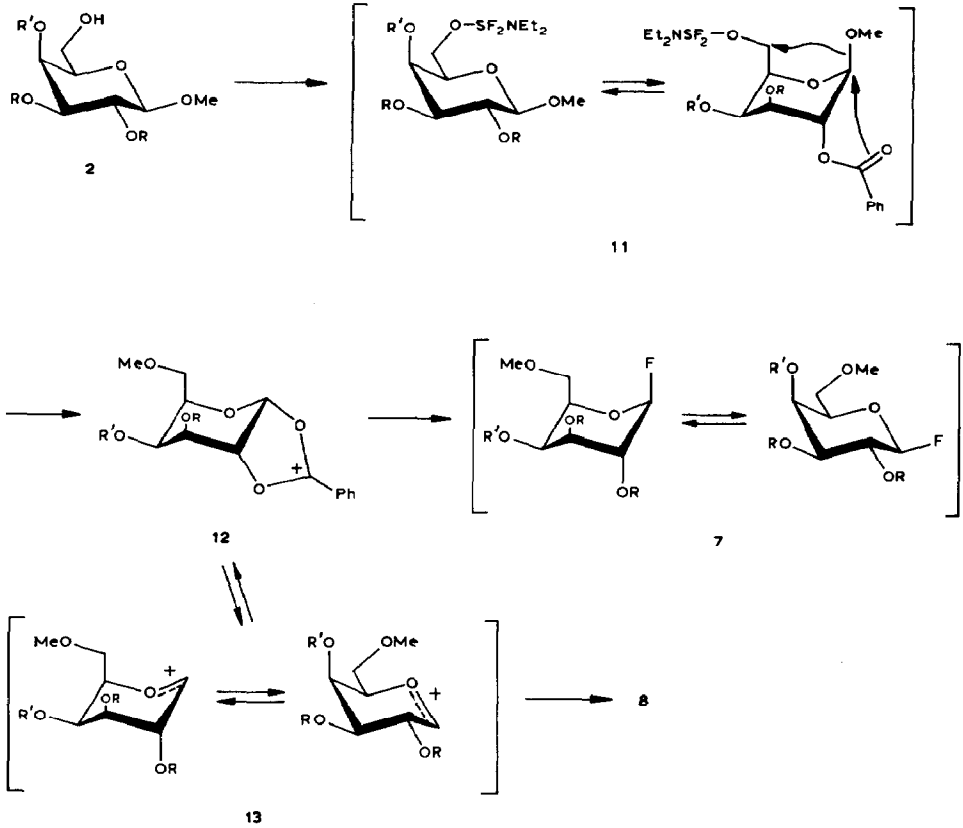


10

A plausible route for the formation of **7** and **8** from **2** involves the sulfoxo derivative[14] **11**. A 1→6 migration of the methoxyl group occurs in the $^1C_4$ conformation, which is probably augmented by BzO-2 *via* the benzoxonium ion **12**. Nucleophilic attack at C-1 of **12** by a fluoride ion should occur from the less-hindered (β) side, to give the major product **7**. Nucleophilic attack by fluoride ion on the α side of **13** (in equilibrium with **12**) provides a route to the minor product **8**.

Several examples of aglycon migrations are known, but this seems to be the first example of the 1→6 migration of a methoxyl group. Recently 1→2 migrations were described in methyl α-D-mannopyranosides[12a,15] and methyl and benzyl α-L-talofuranosides[16] on attempted fluorination with DAST. A synthetic method based on DAST-induced 1→2 migration in *O*-, *S*-, or *N*-glycosyl derivatives has also been



reported[17]. Earlier examples of methoxyl group migrations include a 1→2 migration in a mannopyranoside[18], 1→5 migrations in furanosides[19], and 1→4 migrations in gluco- and xylo-pyranosides[20], and in an acyclic ribose dimethyl acetal[21].

When **2** was treated[3] with trifluoromethanesulfonic anhydride and TASF, the main product was the alkene **9** (79%), and only 16% of the desired 6-deoxy-6-fluorogalabioside[2] **10** was obtained. The double bond in **9** was revealed by the ^{1}H-n.m.r. spectrum (δ 4.95 and 4.90 for H-6,6), by the chemical shifts (δ 151 and 101,

TABLE II

^{19}F-N.M.R. DATA FOR **7** AND **8**.

Compound	*Φ (p.p.m.)*	*J (Hz)*				
	F-1	*H-1,F*	*C-1,F*	*H-1,H-2*	*H-2,F*	*C-3,F*
7	142	53	218	6.1	10.8	8.8
8	150	54	227	2.7	23.0	2.6

respectively) of the C-5 and C-6 resonances, and by the i.r. absorption at 1670 cm^{-1}. The difficulty of 6-fluorination of **1** and **2** prompted the introduction of the fluorine substituent at the monosaccharide level. The preparation of methyl 6-deoxy-6-fluoro-β-D-galabioside by that approach and the preparations of methyl 6-*O*-methyl- and 6-deoxy-β-D-galabioside (from **1** and **2**, respectively) will be reported separately[2].

EXPERIMENTAL

General methods. — N.m.r. spectra were recorded with a Varian XL-300 spectrometer. ^1H- and ^{13}C-n.m.r. spectra were obtained for solutions in $CDCl_3$ (internal Me_4Si) and ^{19}F-n.m.r. spectra were obtained for solutions in $CDCl_3$ and $(CD_3)_2SO$ (external trifluoroacetic acid). ^{19}F-chemical shifts (Φ) are expressed in p.p.m. upfield from the signal for $CFCl_3$. The assignment of the ^1H-chemical shifts and coupling constants and of the ^{13}C-chemical shifts for **4**, especially in the 3,6-anhydropyranosidic ring, were accomplished by a combination of 2D-HOMCOR, 2D-HETCOR, n.O.e., and DEPT experiments. The assignment of the ^1H- and ^{13}C-chemical shifts for **9**, especially for the alkene part, were accomplished by 2D-HETCOR and DEPT experiments. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. T.l.c. was performed on Kieselgel 60 F_{254} (Merck) with detection by u.v. light or charring with sulfuric acid. Column chromatography was performed on Kieselgel 60 (Merck, 230–240 mesh). Organic solutions were dried over Na_2SO_4. The preparation of methyl 2,3-di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-β-D-galactopyranoside (**1**) and methyl 2,3-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-β-D-galactopyranoside (**2**) are reported elsewhere[2].

Methyl 3,6-anhydro-2-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl)-β-D-galactopyranoside (**3**). — DAST (18.4 μL, 151 μmol) was added to a solution of **1**[2] (45 mg, 50 μmol) in dry dichloromethane (0.75 mL), under dry nitrogen, at −45°. The solution was allowed to attain room temperature and then cooled to −45°, methanol (100 μL) was added, and the solution was allowed to attain room temperature and then concentrated. Column chromatography (ethyl acetate–heptane, 1:4) of the residue gave **3** (29 mg, 73%), as a syrup, $[\alpha]_D^{25}$ +23° (*c* 0.9, chloroform). ^1H-N.m.r. data ($CDCl_3$): δ 4.97 (d, 1 H, *J* 3.7 Hz, H-1′), 4.05 (bt, 1 H, *J* 6.8 Hz, H-5′), 4.02 (dd, 1 H, *J* 10.2 and 3.4 Hz, H-2′), 3.88 (dd, 1 H, *J* 10.2 and 2.7 Hz, H-3′), 3.67 (d, 1 H, *J* 4.9 Hz, H-2 or H-3), 3.53 (dd, AB-type, 1 H, *J* 9.5 and 6.1 Hz, H-6′), 3.49 (dd, AB-type, 1 H, *J* 9.5 and 6.9 Hz, H-6′), 3.36 (s, 3 H, MeO).

Anal. Calc. for $C_{48}H_{52}O_{10}$: C, 73.1; H, 6.6. Found: C, 73.5; H, 6.6.

Methyl 2-O-acetyl-3,6-anhydro-4-O-(2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl)-β-D-galactopyranoside (**4**). — Pd/C (10%, 30 mg) was added to a solution of **3** (20 mg, 25 μmol) in acetic acid (1.0 mL). The mixture was hydrogenated for 1 h at atmospheric pressure, then filtered through Celite, and concentrated. Conventional acetylation of the residue gave **4** (12.6 mg, 91%), as a syrup with sufficient

purity to obtain the following data. N.m.r. data ($CDCl_3$): ^1H, δ 5.44 (dd, 1 H, J 3.4 and 1.0 Hz, H-4′), 5.33 (d, 1 H, J 3.4 Hz, H-1′), 5.27 (dd, 1 H, J 11.0 and 3.3 Hz, H-3′), 5.08 (dd, 1 H, J 11.0 and 3.5 Hz, H-2′), 5.00 (d, 1 H, J 4.8 Hz, H-2, 39% n.O.e. on saturation of H-1), 4.53 (d, 1 H, J 4.8 Hz, H-3), 4.45 (s, 1 H, H-1), 4.31–4.23 (m, 4 H, H-4,5,6,5′), 4.12 (dd, AB-type, 1 H, J 11.4 and 5.6 Hz, H-6′), 4.04 (dd, AB-type, 1 H, J 11.4 and 7.2 Hz, H-6′), 3.90 (dd, 1 H, J 9.8 and 2.9 Hz, H-6*exo*[5]), 3.41 (s, 3 H, MeO), 2.14, 2.11, 2.08, 2.06, and 1.99 (5 s, each 3 H, 5 Ac); ^{13}C, δ 100.5 (C-1), 96.3 (C-1′), 78.4, 76.6 (C-3), 75.4, 73.4 (C-2), 70.6 (C-6), 67.9 (C-2′ and C-4′), 67.2 (C-3′), 66.9, 61.7 (C-6′), 56.0 (MeO).

*2,3-Di-*O*-benzoyl-6-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-galactopyranosyl)-β-*D*-galactopyranosyl fluoride* (**7**) *and 2,3-di-*O*-benzoyl-6-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-galactopyranosyl)-α-*D*-galactopyranosyl fluoride* (**8**). — DAST (169 μL, 1.39 mmol) was added to a solution of **2**[2] (570 mg, 0.616 mmol) in dry dichloromethane (10 mL), under dry nitrogen, at −45°. Methanol (200 μL) was added to the solution after 3 h at room temperature. The resulting solution was concentrated after 1 h at room temperature and the residue was subjected to column chromatography (ethyl acetate–heptane, 1:5 then 1:4) to give **7** (290 mg, 51%) and **8** (54 mg, 9.5%) as syrups.

Compound **7** had $[\alpha]_D^{25}$ +78° (*c* 2, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.81 (ddd, 1 H, $J_{H\text{-}2,F}$ 10.8 and J 10.0 and 6.1 Hz, H-2), 5.50 (dd, 1 H, $J_{H\text{-}1,F}$ 52.7 and J 6.1 Hz, H-1), 5.28 (bdd, 1 H, J 10.0 and 2.9 Hz, H-3), 4.91 (d, 1 H, J 3.2 Hz, H-1′), 4.39 (bs, 1 H, H-4), 4.30 (bdd, 1 H, J 5.2 and 8.9 Hz, H-6′), 4.02 (bt, 1 H, J 6.3 Hz, H-5), 3.82 (dd, AB-type, 1 H, J 10.1 and 5.3 Hz, H-6), 3.68 (dd, AB-type, 1 H, J 10.1 and 7.3 Hz, H-6), 3.41 (t, 1 H, J 8.8 Hz, H-6′), 3.15 (s, 3 H, MeO), 3.08 (dd, 1 H, J 8.5 and 5.2 Hz, H-5′); ^{13}C, δ 107.1 (d, $J_{C\text{-}1,F}$ 218 Hz, C-1), 100.2 (C-1′), 78.8, 76.5, 74.9, 74.7, 74.5 (d, $J_{C\text{-}4,F}$ 3.7 Hz, C-4), 74.0, 73.9, 73.0, 72.6 (d, $J_{C\text{-}3,F}$ 8.8 Hz, C-3), 72.5, 70.6, 69.8, 69.7 (d, $J_{C\text{-}2,F}$ 26 Hz, C-2), 67.7, 58.9 (OCH_3); ^{19}F [$(CD_3)_2SO$], Φ 142.1 (bd, $J_{F,H\text{-}1}$ 51.8 Hz, F-1).

Anal. Calc. for $C_{55}H_{55}FO_{12}$: C, 71.3; H, 6.0. Found: C, 71.0; H, 6.0.

Compound **8** had $[\alpha]_D^{25}$ +113° (*c* 1.8, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.97 (dd, 1 H, $J_{H\text{-}1,F}$ 54.3 and J 2.7 Hz, H-1), 5.77 (ddd, 1 H, $J_{H\text{-}2,F}$ 23.0 and J 11.0 and 2.7 Hz, H-2), 5.63 (dd, 1 H, J 11.0 and 2.6 Hz, H-3), 4.94 (d, 1 H, J 3.0 Hz, H-1′), 4.48 (bd, 1 H, J 2.2 Hz, H-4), 4.36 (bt, 1 H, J 6.5 Hz, H-5), 4.27 (bdd, 1 H, J 9.0 and 5.4 Hz, H-6′), 3.76 (dd, AB-type, 1 H, J 10.0 and 6.4 Hz, H-6), 3.53 (dd, AB-type, 1 H, J 10.0 and 6.8 Hz, H-6), 3.37 (t, 1 H, J 8.7 Hz, H-6′), 3.15 (s, 3 H, MeO), 2.95 (dd, 1 H, J 8.4 and 5.3 Hz, H-5′); ^{13}C, δ 105.0 (d, $J_{C\text{-}1,F}$ 227 Hz, C-1), 100.2 (C-1′), 78.8, 76.4, 75.4, 74.9, 74.6, 74.3, 73.0, 72.4, 72.1 (d, $J_{C\text{-}3,F}$ 2.6 Hz, C-3), 70.5, 70.1, 69.8, 68.3 (d, $J_{C\text{-}2,F}$ 24.3 Hz, C-2), 67.7, 58.8 (OCH_3); ^{19}F, Φ 150.0 (dd, $J_{F,H\text{-}1}$ 54.9, $J_{F,H\text{-}2}$ 24.4 Hz, F-1).

Anal. Calc. for $C_{55}H_{55}FO_{12}$: C, 71.3; H, 6.0. Found: C, 71.0; H, 6.0.

*Methyl 2,3-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-galactopyranosyl)-α-*L*-arabino-hex-5-enopyranoside* (**9**) *and methyl 2,3-di-*O*-benzoyl-6-deoxy-6-fluoro-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-galactopyranosyl)-β-*D*-galactopyranoside*

(**10**). — Trifluoromethanesulfonic anhydride (88 μL, 0.54 mmol) was added to a solution of **2**[2] (200 mg, 0.216 mmol) and pyridine (52 μL, 0.65 mmol) in dichloromethane (4 mL) at −15°. After 20 min, the solution was diluted with dichloromethane (16 mL), washed with ice-cold 0.5M hydrochloric acid (8 mL) and water (8 mL), dried, and concentrated[22]. Tris(dimethylamino)sulphonium difluorotrimethylsilicate (TASF, 179 mg, 0.649 mmol) was added to a solution of the residue in dichloromethane (5 mL) at −15° under dry nitrogen. After 1 h at room temperature, the solution was diluted with dichloromethane (15 mL), washed with aqueous sodium hydrogencarbonate (7.5 mL) and water (7.5 mL), dried, and concentrated. Column chromatography (ether–toluene, 1:22) of the residue gave **9** (155 mg, 79%) and **10**[2] (33 mg, 16%).

Compound **9** had $[\alpha]_D^{25}$ +56° (*c* 1.2, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.83 (dd, 1 H, *J* 5.5 and 7.7 Hz, H-2), 5.51 (dd, 1 H, *J* 7.7 and 3.4 Hz, H-3), 5.13 (d, 1 H, *J* 3.5 Hz, H-1′), 4.95 (bs, 1 H, H-6), 4.90 (bs, 1 H, H-6), 4.83 (d, 1 H, *J* 5.5 Hz, H-1), 4.69 (1 H, H-4), 4.07 (dd, AB-type, 1 H, *J* 10.1 and 3.5 Hz, H-2′), 3.95 (dd, AB-type, 1 H, *J* 10.1 and 2.6 Hz, H-3′), 3.93 (bt, 1 H, *J* 6.8 Hz, H-5′), 3.76 (bd, 1 H, *J* 2.0 Hz, H-4′), 3.52 (s, 3 H, MeO), 3.29 (dd, AB-type, 1 H, *J* 9.2 and 6.6 Hz, H-6′), 3.25 (dd, AB-type, 1 H, *J* 9.2 and 6.4 Hz, H-6′); ^{13}C, δ 150.6 (C-5), 101.6 (C-1), 101.0 (C-6), 95.3 (C-1′), 78.3 (C-3′), 76.1 (C-2′), 75.4 (C-4′), 71.2 (C-3), 71.0 (C-4), 69.8 (C-5′), 69.1 (C-2), 68.5 (C-6), 55.8 (OCH_3). I.r. data (neat): 1670 (C=C st).

Anal. Calc. for $C_{55}H_{54}O_{12}$: C, 72.8; H, 6.0. Found: C, 72.8; H, 6.0.

ACKNOWLEDGMENTS

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