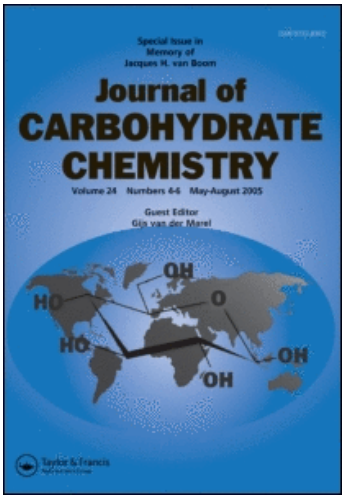

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SYNTHESIS OF THE SODIUM SALTS OF METHYL α-L-FUCOPYRANOSIDE 2-, 3-, AND 4-SULFATES

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ABSTRACT

The sodium salts of the isomeric methyl α-L-fucopyranoside 2-, 3- and 4- sulfates have been prepared from methyl α-L-fucopyranoside **1**. Specific hydroxyl groups, isolated by 4-dimethylaminopyridine-catalyzed tritylation and acetylation of **1**, were sulfated by the pyridine:SO_3 complex.

INTRODUCTION

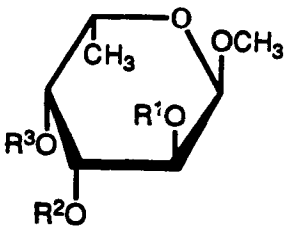
Fucoidan, a polysaccharide extracted from seaweed, is composed primarily of α-(1→2)-linked 4-sulfuryl-L-fucopyranose with occasional branching or sulfation at C-3.[1] It is a mitogen for human lymphocytes,[2] has high antithrombin activity[3] and is an inhibitor of several physiological processes such as the fusion of egg and sperm,[4] binding of lymphocytes to cell surfaces[5] and of laminin and thrombospondin to sulfatides.[6,7] Specifically sulfated methyl L-fucosides may help elucidate the nature of these varied effects. With a similar purpose in mind, Jain and Matta[8,9] have recently described the synthesis of the 3- and 4- sulfates of methyl 2-*O*-α-L-fucopyranosyl-α-L-fucopyranoside.

The synthesis of barium (methyl α-L-fucopyranoside) 2-sulfate prepared via the isopropylidene derivative has been described.[10]

RESULTS AND DISCUSSION

Methyl α-L-fucopyranoside[11] (**1**), lends itself to the isolation of specific hydroxyl groups by tritylation and acetylation because of the low reactivity of the axial *C-4* hydroxyl group. Tritylation of **1** in methylene chloride under reflux, catalyzed[12] by *N,N*-dimethylaminopyridine produced a mixture of **2** and **3**. The isolation of the two triphenylmethyl ethers followed the conditions described[13] for the compounds in the D-series. No 4-*O*-trityl product was detected (TLC). After chromatography, **2** was separated as a crystalline pyridine adduct from which the mono-ethyl alcoholate was obtained. The 3-*O* isomer **3**, which does not form an insoluble pyridine adduct, crystallized as a monohydrate. ^{1}H NMR data for **2** and **3** were in good agreement with those reported for the enantiomers. The crystalline alcoholate of **2** exhibited complex melting behavior: it melted transiently at 118-124 °C, then solidified, and

	R^1	R^2	R^3
1	H	H	H
2	Tr	H	H
3	H	Tr	H
4	Tr	Ac	Ac
5	Ac	Tr	H
6	Ac	Tr	Ac
7	H	Ac	Ac
8	Ac	H	Ac
9	SO_3Na	H	H
10	H	SO_3Na	H
11	H	H	SO_3Na



melted sharply at 133 °C. This mp is somewhat higher than the reported value[14] (127-128 °C), and markedly higher than that reported[13] for the enantiomer (68-70 °C). The specific rotation found for **2**, -55.6°, compared well with the published values, (-58.0°) and (+55.5°). Although the specific rotation of **3**, -107°, did not mirror the value reported[13] for the enantiomer, (+81.4°), the melting points were in good agreement, (71-73 °C) vs (71-74 °C).

Acetylation of each of the trityl compounds **2** and **3** produced the crystalline acetates **4**, **5** and **6**, each, in approximately 60% yield. The two hydroxyl groups of **2** are rapidly acetylated with no indication (TLC) of the transient accumulation of a monoacetylated intermediate. The ^{1}H NMR spectrum of **4** was consistent with that reported[13] for the enantiomer and the specific rotation, -40.4°, was in good agreement with the reported values, -37.5° and +38.0°. As in the case of **2**, significant divergence of melting points,[14,13] particularly for the enantiomer was observed, 219-220 °C vs 208-210 °C and 172-174 °C. The acetylation of **3** rapidly produced the monoacetylated derivative **5.** In the presence of a large excess of acetic anhydride, **5** is slowly converted to the diacetyl derivative **6**. The previously described[13] acetylation of **3** in pyridine at room temperature gave only the monoacetyl derivative which was not fully characterized.

Detritylation of **4** and **6**, producing methyl 3,4-di-*O*-acetyl- and methyl 2,4-di-*O*-acetyl α-L-fucopyranoside, **7** and **8**, respectively, was effected by boron trifluoride catalyzed transetherification, as described by Dax et. al.[15] The reaction was complete (TLC) within 20 min. Acetyl migration did not occur during detritylation. However, attempts to purify **8** by crystallization from hot aqueous ethanol or by silica gel chromatography resulted in the appearance of a new chromatographic spot of low intensity. The newly formed material, which moved slightly in advance of **8**, was not further investigated. The *cis* nature of the C-3 and C-4 hydroxyl groups suggests that the contaminant could be the 2,3-diacetate. Exposing **7** to silica did not result in acetyl migration to the *trans* C-2 hydroxyl group. Migration in aqueous pyridine from *O*-4 to *O*-3 has been observed[16] in glucosamine derivatives in which the relevant hydroxyl groups have a *trans* relationship.

The di-*O*-acetylated fucosides **7** and **8** were sulfated with pyridine:SO_3 complex. The reactions were complete in 30 minutes. During isolation of the product, care was exercised in adjusting the pH to avoid the alkaline hydrolysis of acetyl groups. The sulfated acetates were not isolated. After deacetylation, the sodium salts **9** and **10** were each crystallized from 95% ethanol in 60-70% yield.

The 3-*O*-trityl-2-*O*-acetyl derivative **5** was sulfated with pyridine:SO_3 complex (freshly purified to minimize the presence of the acidic impurity, pyridine sulfate) and subsequently detritylated by acidifying the methanolic solution of the product with sulfonic acid resin AG-50X8 (H^+ form). After deacetylation (Zemplén), the product **11** was crystallized in 89% yield. Comparison of the ^{1}H NMR spectra of the three isomeric sulfates with that of methyl α-D-fucopyranoside[17] revealed that the sulfate group caused a downfield shift of the proton signal in the $HCOSO_3Na$ group of approximately 0.7, 0.8 and 1.1 ppm in **9, 10,** and **11** respectively. Similar deshielding effects of 0.6-0.7 ppm

have been reported[18] in galactose sulfates. There too, the effect was greatest for the proton associated with the axial C-4 sulfate.

EXPERIMENTAL

General Procedures. Melting points were determined on a Kofler hot stage. Optical rotations were measured with a Perkin-Elmer automatic polarimeter, Model 241 MC. Thin layer chromatography (TLC) was performed on 0.2 mm thick layers of Silica Gel 60 with fluorescent indicator on aluminum (E. Merck, Darmstadt, Germany), using solvent mixtures as follows: *A*, acetone-benzene, 1:4; *B*, ethyl acetate-carbon tetrachloride, 1:4; *C*, hexane-ethyl acetate, 1:1; *D*, ethyl acetate-benzene, 1:1. Carbohydrate derivatives were detected by charring with 5% sulfuric acid in ethanol. Tritylated compounds were revealed as yellow spots without warming or before the onset of charring. Column chromatography was performed on Silica Gel 60, particle size 0.035-0.070 mm (Fluka, Buchs, Switzerland). Pyridine (0.025%) was added to all solvents used in the chromatographic purification of trityl ethers. ^{1}H NMR spectra were recorded at 25 °C and 300 MHz using a Varian FX 300 or Gemini spectrometer; chemical shifts (δ) are expressed downfield from the signal of tetramethylsilane or sodium 3-(trimethylsilyl) proprionate. Solvents were stored over molecular sieve 4 Å. Solutions in organic solvents were dried over sodium sulfate and evaporations were conducted under reduced pressure and <40 °C. Boron trifluoride-methanol complex (12% in methanol) was purchased from Aldrich, Milwaukee, U.S.A.. Pyridine:SO_3 complex was freshly purified by trituration with ice water to dissolve pyridine sulfate. The insoluble pyridine complex was washed on a Büchner filter with cold chloroform, pressed dry with heavy filter paper and dried in the cold over phosphorus pentoxide *in vacuo*. Elemental analysis was performed by Atlantic Microlab, Inc., Norcross, Georgia.

Methyl 2-*O*-triphenylmethyl-α-L-fucopyranoside (2) and Methyl 3-*O*-Triphenylmethyl-α-L-fucopyranoside (3). A mixture of **1** (17.4 g, 97.8 mmol), triethylamine (56 mL, 400 mmol), triphenylmethyl chloride (60 g, 215 mmol) and *N,N*-dimethylaminopyridine (1.22 g, 10 mmol) in methylene chloride (180 mL) was refluxed under anhydrous conditions for 96 h. After cooling (25 °C), water (100 mL) was added and the solution was washed sequentially, twice each time, with 100 mL portions of water, saturated ammonium chloride and water. The solution was dried and the solvent was removed to produce a thick syrup which contained **2** and **3** as the only carbohydrate derivatives (TLC, solvent *A*). A considerable amount of a non-carbohydrate contaminant containing a trityl group was also present.

A solution of the crude mixture of **2** and **3** in toluene (200 mL) was applied to a silica gel column (45 x 4 cm) and the column was washed first with toluene (1.3 L) and then with acetone-toluene mixtures [1:16 (v/v, 1 L) and 1:4 (v/v 1.5 L)]. The fractions containing a mixture of **2** and **3** were combined and concentrated. The residue, dissolved in hot pyridine (60 mL), provided fine colorless needles of **2** as the pyridine adduct (15 g, 31%). This material (3 g) was repeatedly concentrated with added toluene to remove pyridine, then crystallized from ethanol (10-15 mL) to give the ethanolate. Recrystallization provided the analytical sample of **2**, mp ~118-124 °C, with subsequent solidification and sharp melting at 133 °C, $[\alpha]_D$ -55.6° (*c* 0.72, chloroform); lit[14] mp 127-128 °C, $[\alpha]_D$ -58° (*c* 2.16, chloroform), and mp 68-70 °C, $[\alpha]_D$ +55.5° (*c* 1, chloroform) for the enantiomer.[13] ^{1}H NMR was carried out on a sample from which all but a trace of ethanol of crystallization had been removed under vacuum; ^{1}H NMR ($CDCl_3$) δ 4.06 (bdd, 1 H, $J_{3,2}$ = 9.7 Hz, H-3), 4.01 (d, 1 H, $J_{1,2}$ = 3.4 Hz, H-1), 3.87 (dd, 1 H, $J_{5,Me}$ = 6.6 Hz, H-5), 3.77 (dd, 1 H, H-2), 3.70 (bd, 1 H, H-4), 3.28 (s, 3 H, OMe), 1.18 (d, 3 H, Me).

Anal. Calcd for $C_{26}H_{28}O_5 \cdot C_2H_5OH$: C, 72.08; H, 7.35. Found: C, 72.00; H, 7.35.

The filtrate from the initial crystallization of **2** as the pyridine adduct was concentrated to an oil which was dissolved in hot methanol (40 mL). On the addition of water (15-20 mL) **3** crystallized as the monohydrate (12 g, 28%). Recrystallization from approximately 70% methanol by the same technique produced short polygonal rods of **3**, mp 71-73 °C, $[\alpha]_D$ -107° (*c* 0.7, chloroform); lit[13] mp 71-74 °C $[\alpha]_D$ +81.4° (*c* 1, chloroform) for the enantiomer; ^{1}H NMR ($CDCl_3$) δ 4.69 (d, 1 H, $J_{1,2}$ = 3.7 Hz, H-1), 4.07 (sextet which collapsed to a dd on the addition of CD_3OD, 1 H $J_{2,3}$ = 9.5 Hz, H-2), 3.86 (dd, 1 H, H-3), 3.43 (dd, 1 H, $J_{5,Me}$ = 6.6 Hz H-5), 3.40 (s, 3 H, OMe), 1.99 (bs, 1 H , H-4), 0.98 (d, 3 H, Me).

Anal. Calcd for $C_{26}H_{28}O_5 \cdot H_2O$: C, 71.21; H, 6.90. Found: C, 71.29; H, 6.87.

Methyl 3,4 Di-*O*-acetyl-2-*O*-triphenylmethyl-α-L-fucopyranoside (4). A solution of **2** (5.04 g, 12 mmol), triethylamine (5.5 mL, 39 mmol), acetic anhydride (3.3mL, 36 mmol) and *N,N*-dimethylaminopyridine (0.15 g, 1.3 mmol) in methylene chloride (40 mL) was refluxed for 1 h. TLC (solvent *C*) indicated that all of the starting material, **2** (R_f 0.2), had been converted to a single product (R_f 0.6). The reaction mixture was washed with water, dried, and the methylene chloride solution was concentrated. The solid residue crystallized as short polygonal rods of **4** from 80% aqueous acetone (4.8 g, 79%). Recrystallization from the same solvent provided the analytical sample: mp 219-220 °C; $[\alpha]_D$ -40.4° (*c* 0.7, chloroform); lit[13] mp 172-174 °C, $[\alpha]_D$ + 38.02° (*c* 1, chloroform) for the enantiomer; ^{1}H NMR ($CDCl_3$) δ 5.43 (dd, 1 H, $J_{3,2}$ = 10 Hz, H-3), 5.11 (bd, 1

H, H-4), 4.02 (m, 1 H, $J_{5,Me}$ = 6.6 Hz, H-5), 3.99 (d, 1 H, $J_{1,2}$ = 3.4 Hz, H-1), 3.84 (dd, 1 H, H-2), 3.27 (s, 3 H, OMe), 1.88 (s, 3 H, OAc), 1.73 (s, 3 H, OAc), 0.99 (d, 3 H, Me).

Anal. Calcd for $C_{30}H_{32}O_7$: C, 71.41; H, 6.40. Found: C, 71.49; H, 6.44.

Methyl 2-*O*-Acetyl-3-*O*-triphenylmethyl-α-L-fucopyranoside (5). A solution of **3** (9.2 g, 21 mmol), triethylamine (4.6 mL, 33 mmol), *N*,*N*-dimethylaminopyridine (0.3 g, 2.5 mmol), and acetic anhydride (3.1 mL, 33 mmol) in methylene chloride (55 mL) was refluxed for 45 m. The solution was washed with water, dried, and the residue obtained after concentration was chromatographed on a silica gel column (49 x 4 cm). Elution with ethyl acetate-carbon tetrachloride (1:10 v/v) gave the desired product **5** which crystallized from 80% aqueous acetone. Recrystallization from 60 % aqueous ethanol afforded pure **5** (6.4 g, 66%): mp 113-114 °C; $[\alpha]_D$ -78.5° (*c* 0.7, chloroform); ^{1}H NMR ($CDCl_3$) δ 5.36 (dd, 1 H, $J_{1,2}$ = 3.7 Hz, H-2), 4.80 (d, 1 H, H-1) 4.10 (dd, 1 H, $J_{2,3}$ = 10 Hz, H-3) 3.48 (dd, 1 H, $J_{5,Me}$ = 6.6 Hz, H-5) 3.24 (s, 3 H, OMe) 2.24 (m, 1 H, H-4) 2.05 (3 H, OAc) 1.02 (d, 3 H, Me).

Anal. Calcd for $C_{28}H_{30}O_6$: C, 72.71; H, 6.54. Found: C, 72.65; H, 6.59.

Methyl 2,4-Di-*O*-acetyl-3-*O*-triphenylmethyl-α-L-fucopyranoside (6). A solution of **3** (4.5 g, 10.7 mmol), triethylamine (6.8 mL, 48 mmol), acetic anhydride (4.8 g, 48 mmol) and dimethylaminopyridine (0.19 g, 1.6 mmol) in methylene chloride (35 mL) was refluxed for 6.5 h. TLC (solvent *C*) revealed that only traces of the monoacetylated derivative **4** were still present. The mixture was added dropwise to 50 mL of ice-water, the organic phase was separated, washed with several portions of water, dried, and concentrated to dryness. The solid, white residue crystallized from approximately 60 mL of 80% aqueous acetone to yield **6** (3.5 g, 65%) as short, blunt needles. Recrystallization from the same solvent gave the analytical sample: mp 184 °C; $[\alpha]_D$ -100° (c 1, chloroform); ^{1}H NMR ($CDCl_3$) δ 5.32 (dd, 1 H, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10 Hz, H-2) 4.83 (d, 1 H, H-1), 4.27 (d, 1 H, H-4) 4.03 (dd, 1 H, H-3), 3.50 (dd, 1 H, $J_{5,Me}$ = 6.4 Hz, H-5), 3.20 (s, 3 H, OMe), 2.25 (s, 3 H, OAc), 1.86 (s, 3 H, OAc), 0.89 (d, 3 H, Me).

Anal. Calcd for $C_{30}H_{32}O_7$: C, 71.41; H, 6.40. Found: C, 71.18; H, 6.45.

Methyl 3,4-Di-*O*-acetyl-α-L-fucopyranoside (7). To a stirred solution of **4** (4 g, 7.9 mmol) in methylene chloride (150 mL), methanol (3.1 mL) and boron trifluoride-methanol complex (5.25 mL, 8.1 mmol) were added. The detritylation was complete after 15 min at room temperature (TLC, solvent *C*). The solution was washed three times with water (25 mL), dried, and concentrated to a semi-crystalline mass. Crystallization from acetone-petroleum ether gave a crude product (2.3 g) which was chromatographed (solvent *C*). Concentration of pooled fractions gave pure crystalline **7**

(1.2 g, 57%). Two recrystallizations from methylene chloride-petroleum ether gave the analytical sample: mp 134 °C; $[\alpha]_D$ -211° (*c* 0.7, chloroform); ^1H NMR ($CDCl_3$) δ 5.22 (d, 1 H, H-4), 5.11 (dd, 1 H, $J_{3,2}$ = 10 Hz, H-3), 4.81 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H-1), 4.08 (dd, 1 H, $J_{5,Me}$ = 6.5 Hz, H-5), 3.91 (dd, 1 H, H-2), 3.44 (s, 3 H, OMe), 2.15 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), 1.14 (d, 3 H, Me).

Anal. Calcd for $C_{11}H_{18}O_7$: C, 50.36; H, 6.91. Found C, 50.33; H, 6.94.

Methyl 2,4-Di-*O*-acetyl-α-L-fucopyranoside (8). To a solution of **6** (6.3 g, 12.5 mmol) in methylene chloride (235 mL), methanol (5.1 mL) and boron trifluoride-methanol complex (8.2 mL, 12.5 mmol) were added. The detritylation was complete in approximately 12 m, (TLC, solvent *C*). The reaction mixture was extracted four times with water (20 mL) and dried. After concentration to ~25 mL, the addition of petroleum ether provided essentially pure **7** as long blunt needles (2.25 g, 69%). Recrystallization from the same solvent gave the analytical sample: mp 95 °C; $[\alpha]_D$ -163° (*c* 1.1, chloroform); ^1H NMR ($CDCl_3$) δ 5.24 (d, 1 H, H-4), 5.00 (dd, 1 H, $J_{2,3}$ = 10 Hz, H-2), 4.90 (d, 1 H, $J_{1,2}$ = 3.6 Hz, H-1), 4.20 (septet which collapsed to a dd on addition of D_2O, 1 H, $J_{2,3}$ = 10.4 Hz, H-3), 4.06 (dd, 1 H, $J_{5,Me}$ = 6.5 Hz, H-5), 3.39 (s, 3 H, OMe), 2.20 (s, 3 H, OAc), 2.15 (s, 3 H, OAc), 1.16 (d, 3 H, Me).

Anal. Calcd for $C_{11}H_{18}O_7$: C, 50.36; H, 6.91. Found: C, 50.17; H, 6.95.

Sodium (Methyl-α-L-fucopyranoside) 2-Sulfate Dihydrate (9). To a solution of **7** (1.2 g, 4.6 mmol) in dry pyridine (11 mL), pyridine:SO_3 complex (0.81 g, 5.1 mmol) was added and the mixture stirred for 1 h at room temperature when no residual **7** was detectable by TLC (solvent *D* , in which sulfated derivatives remain at the origin and di-*O*-acetates move with an Rf of 0.4). The solution was diluted with water and adjusted to pH 7.0 with saturated barium hydroxide. The resulting suspension was repeatedly concentrated with water, adjusting the pH each time to 7, until all of the pyridine had been evaporated. The barium sulfate was removed by centrifugation, washed with water and the combined washings were concentrated to approximately 5 mL, and passed through a column of sulfonic acid resin AG-50X8 (Na^+ form, 18 mL). The resulting eluate containing the sodium salt was repeatedly concentrated to dryness with the addition of methanol. The solid residue, dissolved in methanol (4 mL), was deacetylated (Zemplén) to yield the crystalline dihydrate **9** (1.05 g, 72%). Several recrystallizations from 95% alcohol gave pure **9** as thin right triangles: mp 174 °C (dec); $[\alpha]_D$ -134° (*c* 1.1, H_2O); ^1H NMR (D_2O) δ 5.08 (d, 1 H, $J_{1,2}$ = 3.8 Hz, H-1), 4.42 (dd, 1 H, $J_{2,3}$ = 10 Hz, H-2), 4.09 (dd, 1 H, $J_{5,Me}$ = 6.5 Hz, H-5), 3.95 (dd, 1 H, $J_{3,4}$ = 3.4 Hz, H-3), 3.88 (m, 1 H, H-4), 3.4 (s, 3H, OMe), 1.25 (d, 3 H, Me).

Anal. Calcd for $C_7H_{13}O_8SNa \cdot 2\,H_2O$: C, 26.59; H, 5.41; S, 10.15. Found: C, 26.63; H, 5.36; S, 9.94.

Sodium (Methyl-α-L-fucopyranoside) 3-Sulfate Monohydrate (10). To a solution of **8** (0.7 g, 2.7 mmol) in dry pyridine (15 mL), pyridine:SO_3 complex (0.5 g, 3.1 mmol) was added and the mixture stirred at room temperature. After 1 h, water (30 mL) was added and the mixture worked up as described for the preparation of **9**. The combined aqueous extracts of the barium sulfate precipitate were concentrated, the residue dissolved in methanol (10-15 mL), and deacetylated (Zemplén). The methanol was evaporated and the residue, dissolved in water (3 mL) was passed at 5 °C through a column of cation exchange resin AG-50X8 (H^+ form, 10 mL). The eluate was adjusted to pH 7 with sodium hydroxide (0.2 N), and concentrated to an oil. The addition of ethanol (95%) produced flat, thin rectangular crystals of the product **10** (0.45 g, 56%). Recrystallization provided the analytical sample: mp 161-162 °C (dec); $[\alpha]_D$ -157.4° (*c* 1.3, water); ^1H NMR (D_2O) δ 4.81 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H-1), 4.48 (dd, 1 H, $J_{2,3}$ = 10 Hz, $J_{3,4}$ = 3.1 Hz, H-3), 4.13 (bd, 1 H, H-4), 4.07 (dd, 1 H, $J_{5,Me}$ = 6.5 Hz, H-5), 3.92 (dd, 1 H, H-2), 3.38 (s, 3 H, OMe), 1.23 (d, 3 H, Me).

Anal. Calcd for $C_7H_{13}O_8SNa \cdot H_2O$: C, 28.18; H, 5.07; S, 10.76. Found: C, 28.45; H, 4.91; S, 10.78.

Sodium (Methyl-α-L-fucopyranoside) 4-Sulfate (11). To a solution of **5** (1.4 g, 3 mmol) in dry pyridine (50 mL), pyridine:SO_3 complex [freshly purified, (0.57 g, 3.6 mmol)] was added and the mixture stirred for 1 h at 45 °C. Water (50 mL) was added and the pyridine and inorganic sulfate removed as described for the preparation of **9**. The precipitate of crude sulfated **5** was extracted with methanol. The trityl group was hydrolyzed by slightly acidifying this methanol extract with sulfonic acid resin. After concentrating the extract to ~25 mL, methanol washed sulfonic acid resin, AG-50X8 (H^+ form, 0.4 mL) was added. TLC (solvent *B*) revealed that the trityl group was completely hydrolyzed in 10 m. A sufficient amount of sodium methoxide (0.5 M, 2.5 mL) was added to neutralize the acidity and to catalyze the deacetylation of the sulfated intermediate. After 30 m, the solution was passed, at 5 °C, through a column of the same resin (15 mL) and the pH was readjusted to 7 with aqueous sodium hydroxide (0.2N). The slightly turbid solution was concentrated (5-10 mL). Triphenylmethanol was precipitated by the addition of water (100 mL) and filtered off. The addition of ethanol to the concentrated filtrate produced needles of **11** (0.75 g, 89%). Recrystallization from 95% ethanol provided the analytical sample: mp 184 °C (dec); $[\alpha]_D$ -138.5° (*c* 1.8, water); ^1H NMR (D_2O) δ 4.81 (d, 1 H, $J_{3,4}$ = 3.6 Hz, H-4), 4.61 (m, 1 H, H-1), 4.18 (dd, 1 H, $J_{5,Me}$ = 6.4 Hz, H-5), 3.94 (dd, 1 H, $J_{2,3}$ = 10 Hz, H-2), 3.84 (dd, 1 H, H-3), 3.41 (s, 3 H, O-Me), 1.29 (d, 3 H, Me).

Anal. Calcd for $C_7H_{13}O_8SNa$: C, 30.00; H, 4.67; S, 11.45. Found: C, 30.03; H, 4.68; S, 11.51.

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