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Note

Synthesis of methyl 2-*O*-(sodium α-L-fucopyranosyl 3- and 4-sulfate)-α-L-fucopyranoside*

Rakesh K. Jain and Khushi L. Matta†
Department of Gynecologic Oncology, Roswell Park Cancer Insitute, New York State Department of Health, Elm and Carlton Streets, Buffalo, NY 14263 (U.S.A.)

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In a previous paper[2] in this series, we described the synthesis of L-fucosyl-disaccharides having sulfate groups at C-3 or C-4. Such L-fucosyl-oligosaccharides occur naturally as a part of the structure of fucoidan, a sulfated L-fucose polysaccharide, know to possess anticoagulant acticity[3,4]. This polymer and other sulfated polysaccharides are also known to be inhibitors of various envelope viruses including the human immunodeficiency viruses[5–7]. Thus, in a continuing effort to synthesize well-defined sulfated oligosaccharides that occur as a part of fucoidan, we describe herein the synthesis of two sulfated disaccharides of L-fucose.

A common intermediate, namely, methyl 3,4-di-*O*-benzyl-2-*O*-(2-*O*-benzyl-3,4-*O*-isopropylidene-α-L-fucopyranosyl)-α-L-fucopyranoside (**8**) was utilized for the synthesis of both disaccharides. Methyl 2-*O*-benzyl-3,4-*O*-isopropylidene-1-thio-β-L-fucopyranoside (**3**), which was obtained by the isopropylidenation of methyl 1-thio-β-L-fucopyranoside followed by benzylation with sodium hydride–benzyl bromide, was the key glycosyl donor.

Dejter-Juszynski and Flowers[8] synthesyzed methyl 3,4-di-*O*-benzyl-α-L-fucopyranoside (**6**) in low yield from methyl α-L-fucopyranoside, whereas our synthesis involved the benzylation of known methyl 2-*O*-allyl-α-L-fucopyranoside[9] with subsequent removal of the allyl group. Glycosylation of **6** with methyl 2-*O*-benzyl-3,4-*O*-isopropylidene-1-thio-β-fucopyranoside (**3**) in dichloroethane–*N*,*N*-dimethylformamide, in the presence of cupric bromide–tetrabutylammonium bromide[10], gave methyl 3,4-di-*O*-benzyl-2-*O*- (2-*O*-benzyl-3,4-isopropylidene-β-L-fucopyranosyl) -α-L-fucopyranoside (**7**) and methyl 3,4-di-*O*-benzyl-2-*O*-(2-*O*-benzyl-3,4-*O*-isopropylidene-α-L-fucopyranosyl)-α-L-fucopyranoside (**8**) in 27 and 41% yield, respectively, after column chromatographic purification. The ^{1}H-n.m.r. spectra of **7** and **8** were in accord with the structures assigned. Cleavage of the isopropylidene group of **8** with acetic acid gave, in

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† To whom correspondence should be addressed.

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high yield, compound **9**. This was converted into its 3,4-(ethyl orthoacetate) which was hydrolyzed with acetic acid to give a key intermediate, methyl 2-*O*-(4-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-3,4-di-*O*-benzyl-α-L-fucopyranoside (**10**), in 81% yield. The ^{1}H-n.m.r. spectrum of **10** exhibited a low-field chemical shift at δ 4.30 for H-4′, confirming that **10** had been acetylated at O-4. Reaction of **10** with five molar equivalents of sulfur trioxide–pyridine complex in *N,N*-dimethylformamide produced **11** as its sodium salt after cation (Na^+) exchange. *O*-Deacetylation of **11** in methanolic sodium methoxide, followed by hydrogenolysis of the benzyl groups in the presence of palladium-on-carbon then furnished, in 46% yield on the basis of **11**, methyl 2-*O*-(sodium α-L-fucopyranosyl 3-sulfate)-α-L-fucopyranoside (**12**) as the monohydrate after passage through a cation-exchange resin column. The ^{13}C-n.m.r. spectrum of amorphous **11** was in agreement with the structure assigned (Table I).

TABLE I

Proposed ^{13}C-n.m.r. chemical shifts[a]

Carbon atom	*Compound*		
	α-L*Fucp*-(*1*→*2*)-α-L-*Fucp*O*Me*[b]	**12**	**15**
C-1	99.31	99.14	99.19
C-2	75.66	75.57	75.73
C-3	71.38	70.67	71.28
C-4	74.15	74.73	74.74
C-5	69.24	68.72	69.16
C-6	17.99	17.99	17.99
C-1′	99.60	99.52	99.56
C-2′	70.79	69.61	70.73
C-3′	72.17	80.53	70.94
C-4′	74.66	72.95	83.41
C-5′	69.79	69.27	69.24
C-6′	17.99	17.99	18.58
OMe	57.66	57.68	57.70

[a] For solutions in D_2O with Me_4Si as the external standard. [b] Ref. 2.

Regioselective benzylation of diol **9** by the stannylene method in the presence of tetrabutylammonium iodide produced compound **13**, the ^{1}H-n.m.r. spectrum of which was in conformity with the overall structure expected. Sulfation of **13**, in a manner analogous to that described for **10** (to give **11**), gave **14** as its sodium salt. On hydrogenolysis as described for **11** (to give **12**), **14** afforded, in 65% yield, methyl 2-*O*-(sodium α-L-fucopyranosyl 4-sulfate)-α-L-fucopyranoside (**15**) as a monohydrate as described for the preparation of **12**. The ^{13}C-n.m.r. spectrum of **15** was also consistent with the structure assigned (Table I).

EXPERIMENTAL

General methods. — The same methods were used as those previously described[2].

Methyl 3,4-O-isopropylidene-1-thio-β-L-fucopyranoside (**2**). — A solution of methyl 2,3,4-tri-*O*-acetyl-1-thio-β-L-fucopyranoside (**1**, 24 g) in 0.01M sodium methoxide in methanol (300 mL) was stirred for 3 h at room temperature. The base was neutralized with Amberlite IR-120 (H^+) cation-exchange resin, the resin suspension was filtered, and the filtrate concentrated to give a solid residue. To a stirred solution of this solid in *N,N*-dimethylformamide (300 mL) were added 4-toluenesulfonic acid monohydrate (0.35 g) and 2,2-dimethoxypropane (35 mL), and the stirring was continued for 16 h at room temperature. The acid was neutralized with an anion-exchange resin (OH^-), the resin filtered off, and the filtrate concentrated to dryness. The residue was dissolved in chloroform and addition of hexane gave **2** (17 g, 98%) as a low melting solid, $[\alpha]_D^{25}$ −22° (*c* 1.0, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 2.20 (s, 3 H, SMe), 1.50 and 1.35 (each s, 3 H, 3 CMe), and 1.37 (d, 3 H, *J* ~7 Hz, CMe).

Anal. Calc. for $C_{10}H_{18}O_4S$: C, 51.26; H, 7.74. Found: C, 51.32; H, 7.68.

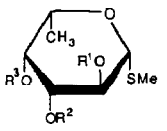
Methyl 2-O-benzyl-3,4-O-isopropylidene-1-thio-β-L-fucopyranoside (**3**). — To a stirred solution of **2** in *N,N*-dimethylformamide (20 mL) was added NaH (0.7 g) portionwise, and the stirring was continued for 0.5 h at room temperature. The mixture was then cooled (~0°; bath), benzyl bromide (2.0 mL) was added, and the stirring was continued for 2 h at room temperature. After careful addition of methanol to decompose excess NaH, the solvent was evaporated and the residue dissolved in chloroform. The solution was washed with water, dried, and concentrated under diminished pressure. The residue was applied to a column of silica gel and eluted with 10% ethyl acetate in hexane to give **3** (2.6 g, 93.8%), amorphous, $[\alpha]_D^{25}$ −1.6° (*c* 1.2, chloroform): ^{1}H-n.m.r. ($CDCl_3$): δ 7.47–7.13 (m, 5 H, arom.), 2.15 (s, 3 H, SMe), 1.43 and 1.33 (each s, 6 H, 2 CMe), and 1.37 (d, 3 H, *J* ~7 Hz, CMe).

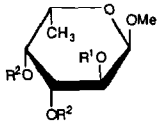
Anal. Calc. for $C_{17}H_{24}O_4S$: C, 62.93; H, 7.46. Found: C, 63.01; H, 7.52.

Methyl 2-O-allyl-3,4-di-O-benzyl-α-L-fucopyranoside (**5**). — To a cold (~0°), stirred solution of **4** (ref. 9; 6.5 g) in *N,N*-dimethylformamide (100 mL) was added NaH (2.0 g), and stirring was continued for 0.5 h at 0°. Benzyl bromide (8.5 mL) was added dropwise and stirring continued overnight at room temperature. After processing as described for **2** (to give **3**), followed by column chromatographic purification on silica gel with 10% ethyl acetate in hexane as the eluent, **4** (9.0 g, 76%) was obtained as a syrup, $[\alpha]_D^{25}$ −47° (*c* 1.6, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.50–7.00 (m, 10 H, arom.), 6.12–5.65 (m, 1 H, $-CH=CH_2$), 3.38 (s, 3 H, OMe), and 1.10 (d, 3 H, *J* ~7 Hz, CMe).

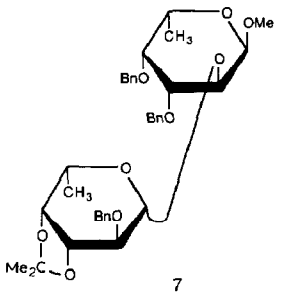
Anal. Calc. for $C_{24}H_{30}O_5$: C, 72.33; H, 7.59. Found: C, 72.52; H, 7.36.

Methyl 3,4-di-O-benzyl-α-L-fucopyranoside (**6**). — A mixture of the 2-*O*-allyl derivative **5** (1.8 g), 10% Pd–C (0.4 g), 4-toluenesulfonic acid monohydrate (0.2 g), methanol (120 mL), and water (30 mL) was refluxed under stirring for 1.5 h. The solid material was then filtered off through Celite and the filtrate concentrated under diminished pressure. The residue was dissolved in chloroform and washed with water, dried, and concentrated. Crystallisation from ether–hexane furnished **6** (1.2 g, 74%), m.p.





1 $R^1 = R^2 = R^3 = Ac$
2 $R^1 = H$; $R^2, R^3 = CMe_2$
3 $R^1 = Bn$; $R^2, R^3 = CMe_2$
4 $R^1 = CH_2CH=CH_2$; $R^2 = H$
5 $R^1 = CH_2CH=CH_2$; $R^2 = Bn$
6 $R^1 = H$; $R^2 = Bn$



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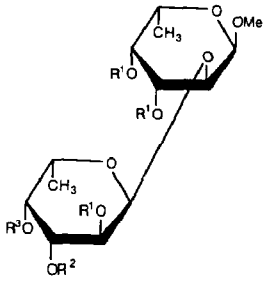

8 $R^1 = Bn$; $R^2, R^3 = CMe_2$
9 $R^1 = Bn$; $R^2 = R^3 = H$
10 $R^1 = Bn$; $R^2 = H$; $R^3 = Ac$
11 $R^1 = Bn$; $R^2 = SO_3Na$; $R^3 = Ac$
12 $R^1 = R^3 = H$; $R^2 = SO_3Na$
13 $R^1 = R^2 = Bn$; $R^3 = H$
14 $R^1 = R^2 = Bn$; $R^3 = SO_3Na$
15 $R^1 = R^2 = H$; $R^3 = SO_3Na$

117–118°, $[\alpha]_D^{25}$ −112° (*c* 0.9, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.40–7.13 (m, 10 H, arom), 3.33 (s, 3 H, OMe), 1.17 (d, $J \sim 7$ Hz, 3 H, CMe); lit.[8] m.p. 92–94°, $[\alpha]_D^{26}$ −57° (*c* 1.1, chloroform).

Methyl 3,4-di-O-benzyl-2-O-[2-O-benzyl-3,4-O-isopropylidene-β- (**7**) *and* α-L-*fucopyranosyl]-*α-L-*fucopyranoside* (**8**). — A solution of methyl 2-*O*-benzyl-3,4-*O*-isopropylidene-1-thio-β-L-fucopyranoside (**3**, 0.84 g, 2.59 mmol), methyl 3,4-di-*O*-benzyl-α-L-fucopyranoside (**6**, 0.72 g, 2.01 mmol) in 5:1 dichloroethane–*N*,*N*-dimethylformamide (60 mL) was stirred for 0.5 h with 4A molecular sieves (4.0 g) under protection from light and moisture, and then tetrabutylammonium bromide (1.3 g, 4.03 mmol) and $CuBr_2$ (0.93 g, 3.99 mmol) were added. The mixture was stirred for 16 h at room temperature and t.l.c. (4:1 hexane–ethyl acetate) showed the presence of two products. The mixture was filtered through Celite, and the solids were thoroughly washed with chloroform. The filtrate and washings were combined, washed with saturated aqueous $NaHCO_3$ and water, dried, and concentrated under diminished pressure. The residue was applied to a

column of silica gel and eluted with a solvent gradient consisting of 20–25% ethyl acetate in hexane. The earlier fractions collected contained the faster-migrating β-D-anomer **7**. On concentration, the fractions corresponding to **7** (0.34 g, 27%) gave an amorphous solid, $[\alpha]_D^{25}$ −65° (*c* 1.3, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.37–7.23 (m, 15 H, arom.), 4.92 (d, *J* 3.2 Hz, H-1), 4.77 (d, *J* 7.7 Hz, H-1′), 3.38 (s, 3 H, OMe), 1.39 and 1.27 (each s, 3 H, CMe), 1.16 (d, 3 H, *J* 6.4 Hz, CMe), and 0.89 (d, 3 H, *J* 6.4 Hz, CMe).

Anal. Calc. for $C_{37}H_{46}O_9$: C, 70.01; H, 7.30. Found: C, 70.25; H, 7.45.

The latter fractions contained the pure α-D anomer **8** (0.51 g, 41%); $[\alpha]_D$ −120° (*c* 1.0, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.37–7.22 (m, 15 H, arom.), 4.86 (d, *J* 3.8 Hz, H-1′), 4.84 (d, 1 H, *J* 3.8 Hz, H-1), 3.40 (s, 3 H, OMe), 1.34 and 1.25 (each s, 3 H, CMe), 1.17 (d, 3 H, *J* 7 Hz, CMe), and 1.15 (d, 3 H, *J* 6.9 Hz, CMe).

Anal. Calc. for $C_{37}H_{46}O_9$: C, 70.01; H, 7.30. Found: C, 70.05; H, 7.28.

*Methyl 3,4-di-*O*-benzyl-2-*O*-(2-*O*-benzyl-α-*L*-fucopyranosyl)-α-*L*-fucopyranoside* (**9**). – Compound **8** (2.6 g) in 60% aqueous acetic acid (75 mL) was stirred for 1.5 h at 50°. Acetic acid was evaporated under diminished pressure, the last traces being removed by coevaporation with several added portions of toluene. The residue was purified in a column of silica gel with 10% acetone in chloroform as eluent. On concentration, the fractions corresponding to **9** gave an amorphous solid (2.2 g, 90%), $[\alpha]_D^{25}$ −128° (*c* 0.5, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.37–7.23 (m, 15 H, arom.), 4.97 (d, *J* 3.8 Hz, H-1′), 4.01 (dd, 1 H, $J_{2',3'}$ 10.5, $J_{3',4'}$ 3.2 Hz, H-3′), 3.69 (d, 1 H, $J_{3',4'}$ 1.9 Hz, H-4′), 3.38 (s, 3 H, OMe), 1.18 (d, 3 H, *J* 7.0 Hz, CMe), and 1.01 (d, 3 H, *J* 6.6 Hz, CMe).

Anal. Calc. for $C_{34}H_{42}O_9$: C, 68.66; H, 7.12. Found: C, 68.77; H, 7.06.

*Methyl 2-*O*-(4-*O*-acetyl-2-*O*-benzyl-α-*L*-fucopyranosyl)-3,4-di-*O*-benzyl-α-*L*-fucopyranoside* (**10**). — To a solution of **9** (1.1 g, 1.85 mmol) in dry benzene (32 mL) was added triethyl orthoacetate (8.0 mL) and 4-toluenesulfonic acid monohydrate (2 mg), and the mixture was stirred for 1.5 h at room temperature. Triethylamine was added and the solution was washed with cold water, dried, and concentrated under diminished pressure to give the 3′-4′-orthoester in quantitative yield. It was dissolved in 80% aqueous acetic acid (50 mL), and the solution was stirred for 1 h at room temperature. Acetic acid was evaporated under diminished pressure, the last traces being removed by coevaporation with several added portions of toluene. The crude product was applied to a column of silica gel. Elution with a solvent gradient consisting of 40–50% ethyl acetate in hexane and evaporation of the fractions corresponding to **10** (0.95 g, 81%) gave an amorphous solid, $[\alpha]_D^{25}$ −118° (*c* 0.4, chloroform); ^{1}H-N.m.r. ($CDCl_3$): δ 7.37–7.23 (m, 10 H, arom.), 4.98 (d, *J* 3.7 Hz, H-1′), 4.30 (d, 1 H, $J_{3',4'}$ 2.2 Hz, H-4′), 4.17 (dd, 1 H, $J_{2',3'}$ 10.5, $J_{3',4'}$ 3.2 Hz, H-3′), 3.38 (s, 3 H, OMe), 2.08 (s, 3 H, OAc), 1.19 (d, 3 H, *J* 7.0 Hz, CMe), and 1.02 (d, 3 H, *J* 6.8 Hz, CMe).

Anal. Calc. for $C_{36}H_{44}O_{10}$: C, 67.90; H, 6.96. Found: C, 67.74; H, 6.65.

*Methyl 3,4-di-*O*-benzyl-2-*O*-(sodium 4-*O*-acetyl-2-*O*-benzyl-α-*L*-fucopyranosyl 3-sulfate)-α-*L*-fucopyranoside* (**11**). — To a stirred solution of **10** (0.9 g, 1.4 mmol) in dry *N,N*-dimethylformamide (25 mL) was added dropwise a solution of SO_3–pyridine complex (1.1 g, 6.9 mmol) in *N,N*-dimethylformamide (20 mL). Stirring was continued for an additional 1.5 h at room temperature, and the excess of reagent was destroyed by

the addition of methanol. The solvent was evaporated, and the residue was dissolved in chloroform and washed with cold water. Evaporation of the solvent gave a syrup which was dissolved in methanol and passed through Amberlite IR-120P (Na^+) cation-exchange resin in methanol. Solvent removal afforded **11** (1.0 g, 96%), $[\alpha]_D^{25}$ −111° (*c* 1.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.49–7.01 (m, 15 H, arom.), 3.37 (s, 3 H, OMe), 1.87 (s, 3 H, OAc), 1.05 (d, 3 H, *J* 7 Hz, CMe), and 0.72 (d, 3 H, *J* 7 Hz, CMe).

Anal. Calc. for $C_{36}H_{43}NaO_{13}S$: C, 58.52; H, 5.87. Found: C, 58.74; H, 6.19.

Methyl 2-O-(sodium α-L-fucopyranosyl 3-sulfate)-α-L-fucopyranoside (**12**). — Compound **11** (0.45 g) was stirred in 0.1 M methanolic sodium methoxide (75 mL) for 16 h at room temperature. The solution was de-ionized with Amberlite IR-120 (H^+) cation-exchange resin, filtered, and concentrated under diminished pressure. The residue was dissolved in 95% ethanol (60 mL) and treated with 10% Pd–C (0.5 g) under H_2 at ~345 kPa for 2 days. The suspension was filtered through a bed of Celite, the solids being thoroughly washed with 20% aqueous ethanol. The filtrate and washings were combined and the solvents evaporated. The residue was purified on a column of silica gel with 13:6:1 (v/v) chloroform–methanol–water as the eluent. The fractions corresponding to **12** were combined and concentrated, and the residue so obtained was dissolved in water and passed through Amberlite IR-120P (Na^+) cation-exchange resin. Lyophilization of the fractions corresponding to **12** gave an amorphous solid (0.12 g, 46%, on the basis of **11**), $[\alpha]_D^{25}$ −157° (*c* 0.5, water); ^{1}H-n.m.r. (D_2O): δ 5.15 (d, *J* 3.8 Hz, H-1′), 5.09 (d, *J* 3.8 Hz, H-1), 3.42 (s, 3 H, OMe), 1.28 (d, 3 H, *J* 6.4 Hz, CMe), and 1.25 (d, 3 H, *J* 6.4 Hz, CMe); for ^{13}C-n.m.r. data, see Table I.

Anal. Calc. for $C_{13}H_{23}NaO_{12}S \cdot H_2O$: C, 35.13; H, 5.67. Found: C, 34.94; H, 5.29.

Methyl 3,4-di-O-benzyl-2-O-(2,3-di-O-benzyl-α-L-fucopyranosyl)-α-L-fucopyranoside (**13**). — A mixture of **9** (0.96 g, 1.6 mmol) and dibutyltin oxide (0.4 g, 1.6 mmol) in benzene (50 mL) was heated for 20 h at reflux temperature with azeotropic distillation of water. The mixture was concentrated to about one-half its volume and, after addition of tetrabutylammonium iodide (0.89 g, 2.4 mmol) and benzyl bromide (0.38 mL, 2.2 mmol), the refluxing was continued for 5 h. Evaporation of the solvent to dryness gave a residue which was purified on a column of silica gel with a solvent gradient consisting of 30–35% ethyl acetate in hexane to afford **13** (1.0 g, 90%), amorphous, $[\alpha]_D^{25}$ −97° (*c* 0.9, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.43–7.11 (m, 20 H, arom.), 3.38 s, 3 H, OMe), 1.15 (d, 3 H, *J* ~7 Hz, CMe), and 1.01 (d, 3 H, *J* ~7 Hz, CMe).

Anal. Calc. for $C_{41}H_{48}O_9$: C, 71.91; H, 7.06. Found: C, 71.78; H, 7.07.

Methyl-3,4-di-O-benzyl-2-O-(sodium 2,3-di-O-benzyl-α-L-fucopyranosyl 4-sulfate)-α-L-fucopyranoside (**14**). — Compound **13** (0.9 g, 1.3 mmol) was treated with SO_3–pyridine complex (1.1 g, 6.9 mmol) exactly as described for **10** (to give **11**). After processing as just described for the preparation of **11**, the residue was dissolved in methanol and passed through an Amberlite IR-120P (Na^+) cation-exchange resin column. The fractions corresponding to **14** were concentrated to give an amorphous solid (1.0 g, 97%), $[\alpha]_D^{25}$ −95° (*c* 1.8, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.49–7.01 (m, 20 H, arom.), 3.20 (s, 3 H, OMe), 1.13 (d, 3 H, *J* ~7 Hz, CMe), and 1.03 (d, 3 H, *J* ~7 Hz, CMe).

Anal. Calc. for $C_{41}H_{47}NaO_{12}S$: C, 62.58; H, 6.02. Found: C, 62.24; H, 6.07.

Methyl 2-O-(sodium α-L-fucopyranosyl 4-sulfate)-α-L-fucopyranoside (**15**). — Compound **14** (0.9 g) was hydrogenated in the presence of 10% Pd–C (1.0 g) as just described. After purification over a silica gel column with 13:6:1 (v/v) chloroform–methanol–water as the eluent, **15** (0.32 g, 65.6%) was obtained as its sodium salt by passing through Amberlite IR 120-P (Na^+) cation-exchange resin, $[\alpha]_D^{25}$ −155° (*c* 0.6, water); ^{1}H-n.m.r. (D_2O): δ 5.04 (d, *J* 3.8 Hz, H-1′), 4.98 (d, *J* 3.8 Hz, H-1), 3.41 (s, 3 H, OMe), 1.27 (d, 3 H, *J* 6.4 Hz, CMe), and 1.23 (d, 3 H, *J* 6.4 Hz, CMe); for ^{13}C-n.m.r. data, see Table I.

Anal. Calc. for $C_{13}H_{23}NaO_{12}S \cdot H_2O$: C, 35.13; H, 5.67. Found: C, 34.73; H, 5.61.

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REFERENCES

1 A. K. Sarkar, S. M. Pawar, and K. L. Matta, *J. Carbohydr. Chem.*, 1990, in press.
2 R. K. Jain and K. L. Matta, *Carbohydr. Res.*, 208 (1990) 51–58.
3 G. F. Springer, H. A. Wurzel, G. M. McNeal, Jr., N. J. Ansell, and M. F. Doughty, *Proc. Soc. Exp. Biol. Med.*, 94 (1957) 404–409.
4 K. Dobashi, T. Nishino, M. Fujihara, and T. Nagumo, *Carbohydr. Res.*, 194 (1989) 315–320.
5 H. Nakashima, O. Yoshida, T. S. Tochikura, T. Yoshida, T. Mimura, Y. Kido, Y. Motoki, Y. Kaneko, T. Uryu, and N. Yamamoto, *Jpn. J. Cancer Res.*, 78 (1987) 1164–1168.
6 M. Baba, R. Snoeck, R. Pauwels, and E. Declercq, *Antimicrob. Agents Chemother.*, 32 (1988) 1742–1745.
7 M. Baba, M. Nakajima, D. Schols, R. Pauwels, J. Balzarini, and E. Declercq, *Antiviral Res.*, 9 (1988) 335–343.
8 M. Dejter-Juszynskc and H. M. Flowers, *Carbohydr. Res.*, 28 (1973) 61–74.
9 H. H. Baer, F. H. Mateo, and L. Siemsem, *Carbohydr. Res.*, 187 (1989) 67–92.
10 S. Sato, M. Mori, Y. Ito, and T. Ogawa, *Carbohydr. Res.*, 155 (1986) c6-c10.