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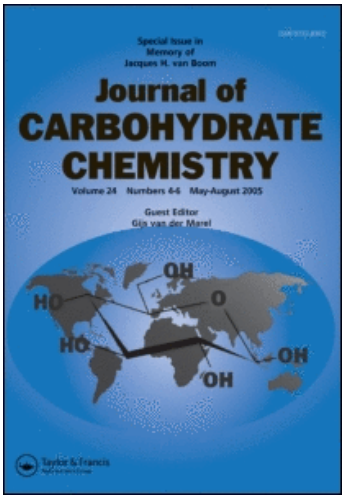

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Studies Directed Towards Stereospecific Synthesis of Oxybiotin, Biotin, and Their Analogs. III. Preparation of Some New 2,5-Anhydro-Xylitol Derivatives

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STUDIES DIRECTED TOWARDS STEREOSPECIFIC SYNTHESIS OF OXYBIOTIN, BIOTIN AND THEIR ANALOGS. III[+]. PREPARATION OF SOME NEW 2,5-ANHYDRO-XYLITOL DERIVATIVES

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ABSTRACT

Some new partially or fully tosylated and/or mesylated 2,5-anhydro-xylitol derivatives have been prepared in this work. Some of them represent the real optically active intermediates in an attempted synthesis of selected (+)-oxybiotin analogs, while the others, being racemic, serve only as easily available model-intermediates.

INTRODUCTION

(+)-Oxybiotin is an oxygen analog of (+)-biotin and shows biotin-like activity in some micro-organisms.[1-4] This can be mainly explained by very similar structural and stereochemical features of both molecules (I and II, Scheme 1). Having in mind that bio-

[+]Part I and II: References 5 and 6.

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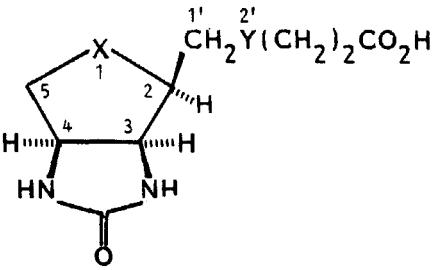

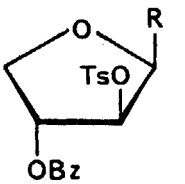

I (+)-Biotin (X = S, Y = CH_2)

II (+)-Oxybiotin (X = O, Y = CH_2)

III 2'-Oxa-analog of II (X = Y = O)

IV 2'-Thia-analog of II (X = O, Y = S)

1 R = 

2 R = $CH(OH)_2$

3 R = CH_2OH

4 R = CH_2OTs

Scheme 1.

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logical activity of some (+)-biotin analogs depends on the length of the side chain (bearing the carboxyl group), one can expect similar biotin activity of (+)-oxybiotin analogs with the side chain containing a heteroatom (O or S) instead of one methylene group (III and IV, Scheme 1).

The main goal of this work was concerned with chemical transformations of D-xylose and xylitol in order to obtain 2,5-anhydro-xylitol derivatives of type 3 and 4, representing suitable intermediates in preparations of (+)-oxybiotin analogs III and IV (Scheme 1).

RESULTS AND DISCUSSION

Ethylene acetal of 2,5-anhydro-4-O-benzoyl-3-O-p-toluenesulfonyl-D-xylose (1, Scheme 1), readily available from D-xylose in five synthetic steps,[5,6] has been used as a starting compound

for preparation of the optically active intermediates 3 and 4. By hydrolysis of compound 1 with CF_3COOH - concd HCl (10:1), at room temperature during 20 h, a hydrated form of the corresponding aldehyde 2 was obtained in a yield of 61%. Due to its instability, compound 2 was reduced, immediately after its brief chromatographic purification, with dimethylamine-borane complex in THF, at room temperature, affording 2,5-anhydro-4-O-benzoyl-3-O-p-toluenesulfonyl-D-xylitol (3, Scheme 1) as the only reaction product. The main advantage of this reducing method consists in a simple and non-aqueous work-up procedure (see experimental part). Finally, compound 3 was tosylated under the standard reaction conditions (tosyl chloride in pyridine at room temperature), whereupon the corresponding ditosylate 4 was obtained in a 90% yield.

Compound 3 represents a key intermediate in an attempted stereospecific synthesis of the mentioned 2'-oxa-analog of (+)-oxybiotin (III, Scheme 1), while compound 4 represents a suitable starting material for the preparation of 2'-thia-analog IV (Scheme 1). In addition, compounds 3 and 4, in respect to chiral and topological properties, are well suited for stereospecific introduction of C-3 and C-4 nitrogen functions,[7] needed for final ureido system building.

Since the overall synthesis of compound 4 was achieved in eight synthetic steps from D-xylose, we decided (for the purpose of model study) to synthesize in only two steps the racemic equivalent of 4 starting from xylitol. For this purpose we have used some well known general principles, namely the readiness with which most known pentitols and hexitols intramolecularly close to give five-membered anhydro-rings.[8-17]

In this work, by using quite mild reaction conditions, we developed an original procedure for converting xylitol into all possible partially and fully tosylated (mesylated) 2,5-anhydro-derivatives 5 - 9 (Scheme 2).

Thus, partial tosylation of xylitol with 2 molar equivalents of tosyl chloride in pyridine at 40 °C for 2 h gave 1-tosylate 5 as

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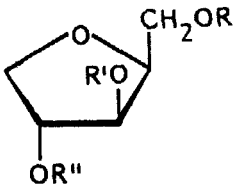

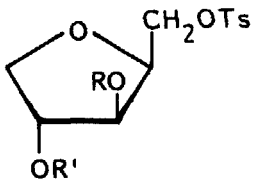

5 R = Ts, R' = R" = H

6 R = R' = Ts, R" = H

7 R = R" = Ts, R' = H

8 R = R' = R" = Ts

9 R = R' = R" = Ms

4' R = OTs
R' = Bz

10 R = Bz
R' = Ts

Scheme 2.

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the main reaction product (56%). On the other hand, 3 molar equivalents of tosyl chloride in pyridine at -20 °C for 7 days gave 1,3-di-tosylate 6 (33%), 1,4-di-tosylate 7 (26%) and tri-tosylate 8 (4%). Finally, tosylation (or mesylation) of xylitol with 5 molar equivalents of tosyl chloride (mesyl chloride) in pyridine, at room temperature, gave tri-tosylate 8 in a yield of 75% (or tri-mesylate 9 in 60% yield). Compound 8 was synthesized earlier[18] but in a yield of only 25%.

Structures of compounds 6 and 7 were deduced from their ^{1}H NMR spectra. Compound 6 gives a first order ^{1}H NMR spectrum. By deuteration, the signal at 2.57 ppm disappears, while the multiplet at 4.49 ppm (dddd) is changed into a simpler multiplet (ddd), due to a loss $^3J_{H\text{-}4,OH}$ (4.2 Hz). This proves the presence of a free hydroxyl group at C-4. The signal at 4.74 ppm (dd), with coupling constants of 1.8 and 4.2 Hz (whose multiplicity is not changed by deuteration) is due to H-3 (bound to the C-3 which bears the tosyloxy-group).

In the ^{1}H NMR spectrum of compound 7 there is a doublet at 2.62 ppm, which disappears upon addition of D_2O.

Simultaneously, the multiplet at 4.43 ppm was simplified. Indeed, the signal at 4.43 (after deuteration) involving two coupling constants (3.6 and 1.9 Hz) proves the presence of a free hydroxyl group at C-3. The signal at 4.83 ppm involves three coupling constants (1.9, 2.1 and 4.8 Hz). This signal corresponds to H-4; since it is not changed by deuteration, the hydroxyl group at C-4 is tosylated.

By using standard synthetic procedure (benzoyl chloride in pyridine at room temperature) compounds 6 and 7 were converted into the corresponding 4-O-benzoyl and 3-O-benzoyl derivatives (4' and 10; Scheme 2). Finally, by comparing ^{1}H NMR and IR spectra of optically active compound 4 (Scheme 1) and racemic compounds 4' and 10 (Scheme 2), it turned out that 1,3-ditosylate 4 structurally corresponds to product 4' (bearing in mind that 4 is a D-form while 4' is a D,L-form).

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EXPERIMENTAL

General procedures - IR Spectra have been recorded with a Perkin-Elmer 457 spectrophotometer and band positions (ν_{max}) are given in cm^{-1}. NMR Spectra have been recorded with a Varian 60 A and a Bruker WP 200 SY instruments, using $CDCl_3$ solutions and tetramethylsilane as an internal standard. Chemical shifts (δ) are given in ppm values. Mass spectra were taken on a VG-7035 mass spectrometer, at 70 eV (first number denotes m/e value, while ion abundances were given in parentheses). Melting points were determined using a Büchi SMP-20 apparatus and were not corrected. Optical rotations were measured on a Polamat A (Karl Zeiss - Jena) polarimeter in chloroform solutions at 25°C.

2,5-Anhydro-4-O-benzoyl-3-O-p-toluenesulfonyl-D-xylose hydrate (2). - A solution of compound 1 (ref. 5, 6; 5 g, 11 mmol) and concd HCl (3 mL) in trifluoracetic acid (30 mL) was left at room temperature for 20 h. The reaction mixture was neutralized with a solution of $NaHCO_3$ (10%; 350 mL), to pH 7-8.

The resulting suspension was extracted with methylene chloride (4×50 mL) and the combined extracts were washed with water (to pH 6-7) and dried (Na_2SO_4). After removal of solvent, a yellow oil remained. The crude product was chromatographed on a column of silica gel (30 g, C_6H_6-EtOAc 9:1) whereupon the pure compound 2 was obtained (2.87 g, 61%) as a colourless unstable syrup: $[\alpha]_D$ - 76.04° (c 0.89); IR (film) 3480-3440 (OH), 1730 (C=O), 1370 (as S=O), 1195-1180 (sym S=O).

2,5-Anhydro-4-O-benzoyl-3-O-p-toluenesulfonyl-D-xylitol (3). - A solution of compound 2 (2.87 g, 7 mmol) and dimethylamine-borane complex (0.43 g, 7.3 mmol) in tetrahydrofuran (80 mL) was stirred at room temperature for 2 h. The reaction mixture was concentrated to dryness and then co-distilled with methanol (3×30 mL). The dry residue was crystallized from di-isopropyl ether affording the pure product 3 as colourless crystals: mp 108-9 °C (1.46 g, 53%); IR (KBr) 3480 (OH), 1700 (C=O); ^{1}H NMR δ 2.37 (s, 3H, CH_3 from Ts), 2.84 (s, 1H, OH), 3.74-3.98 (several signals, 3H, H-2, H-5a, H-5b), 4.20-4.43 (several signals, 2H, H-1a, H-1b), 5.15 (dd, 1H, $J_{3,4}$ = 1.47 Hz, $J_{3,2}$ = 3.9 Hz, H-3), 5.28-5.35 (m, 1H, H-4), 7.77-7.96 (several signals, 10H from arom. rings); ^{13}C NMR δ 21.60 (CH_3 from Ts), 60.02 (C-1), 71.06 (C-5), 77.30 (C-3), 79.99 (C-4), 81.87 (C-2), 127.72-145.41 (C-atoms from arom. rings), 164.67 (C=O).

2,5-Anhydro-4-O-benzoyl-1,3-di-O-p-toluenesulfonyl-D-xylitol (4). - Compound 3 (0.20 g, 0.30 mmol) and p-toluenesulfonyl chloride (0.146 g, 0.76 mmol) in dry pyridine (10 mL) were left at room temperature for 24 h. The reaction mixture was then poured onto ice (20 g) acidified with diluted HCl (1:1, 50 mL), and resulting suspension was extracted with chloroform. The combined extracts were washed with water, then with saturated $NaHCO_3$ solution and dried (Na_2SO_4). After removal of solvent, crude product 4 remained. Chromatographic purification on a column of silica gel (15 g, hexane-acetone 7:3) and crystallization from methanol gave pure compound 4 (0.25 g, 90%); mp 65 °C, $[\alpha]_D$-51.11° (c 1.29); IR (KBr) 1730

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(C=O), 1600 (C=C, arom.), 1370 (as S=O), 1270-1180 (sym S=O); ^{1}H NMR δ 2.41 (s, 3H, CH_3 from Ts), 2.44 (s, 3H, CH_3 from Ts), 3.81 (dd, 1H, $J_{5a,4}$ = 2.2 Hz, $J_{5a,5b}$ = 10.7 Hz, H-5a), 4.11-4.38 (several signals, 4H, H-2, H-5b, H-1a, H-1b), 5.04 (dd, 1H, $J_{3,4}$ = 1.7 Hz, $J_{3,2}$ = 3.7 Hz, H-3), 5.49 (ddd, 1H, $J_{4,5a}$ = 2.2 Hz, $J_{4,3}$ = 1.7 Hz, $J_{4,5b}$ = 4 Hz, H-4), 7.30-7.98 (several signals, 13H, from arom. rings).

Anal. Calcd for $C_{26}H_{26}O_9S_2 \times CH_3OH$: C, 56.05; H, 5.19; S, 11.7. Found: C, 56.14; H, 4.95; S, 10.56.

2,5-Anhydro-1-O-p-toluenesulfonyl-D,L-xylitol (5). - Xylitol (10 g, 66 mmol), p-toluenesulfonyl chloride (25.06 g, 130 mmol) and dry pyridine (150 mL) were stirred at 40° C for 2 h. After removal of pyridine in vacuum (oil pump), the residue was co-distilled with toluene to remove last traces of pyridine. The yellow oil that remained was chromatographically separated on a column of silica gel (300 g, $CHCl_3$-Me_2CO-AcOH 8:2:0.05) affording pure product 5 (10.1 g, 56%). An analytical sample obtained after crystallization from hexane-metylene chloride (3:2) had mp 98 °C: IR (KBr) 3440 (OH), 1600 (C=C, arom.), 1370 (as S=O), 1190-1180 (sym S=O); ^{1}H NMR δ 2.45 (s, 3H, CH_3 from Ts), 2.75-3.10 (2H, 2OH), 3.50-4.25 (several signals, 5H), 7.25-7.90 (4H from arom. ring, Ts). Mass spectrum: 270 (M^+-H_2O; 5).

Anal. Calcd for $C_{12}H_{16}O_6S$: C, 50.00; H 5.55; S, 11.10. Found: C, 50.04; H, 5.78; S; 10.73.

2,5-Anhydro-1,3-di-O-p-toluenesulfonyl-D,L-xylitol (6) and 2,5-anhydro-1,4-di-O-p-toluenesulfonyl-D,L-xylitol (7). - Xylitol (10 g, 66 mmol), p-toluenesulfonyl chloride (37.65 g, 187 mmol) and dry pyridine (150 mL) were left at - 20 °C for 7 days. The reaction mixture was then poured onto ice (200 g), acidified with diluted HCl (1:1, 200 mL), and extracted several times with $CHCl_3$. The combined extracts were washed with HCl-H_2O (1:4), saturated $NaHCO_3$, and water, dried and concentrated. Chromatography on a column of silica gel (300 g, CH_2Cl_2-EtOAc 9:1) afforded 6 (9.53 g, 32.8%): mp 144 °C (from benzene);

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7 (7.45 g, 25.7%), mp 107-8 °C (from benzene-hexane); and 8 (1.83 g, 3.95%), mp 109 °C from EtOH (lit.[18] mp 106 °C).

Compound 6: IR (KBr) 3440 (OH), 1600 (C=C, arom.), 1370 (as S=O), 1200-1170 (sym S=O); ^{1}H NMR δ 2.49 (s, 3H, CH_3 from Ts), 2.51 (s, 3H, CH_3 from Ts), 2.57 (d, 1H, exchangeable with D_2O, $J_{4,OH}$ = 4.2 Hz, OH), 3.65 (dd, 1H, $J_{5a,4}$ = 2.9 Hz, $J_{5a,5b}$ = 10.2 Hz, H-5a), 4.02 (d, 2H, 2H-1), 4.11 (dd, 1H, $J_{5b,4}$ = 5 Hz, $J_{5b,5a}$ = 10.2 Hz, H-5b), 4.26 (dt, 1H, $J_{2,3}$ = 4.2 Hz, $J_{2,1}$ = 6 Hz, H-2), 4.49 (m, 1H, H-4), 4.74 (dd, 1H, $J_{3,4}$ = 1.8 Hz, $J_{3,2}$ = 4.2 Hz, H-3), 7.42-7.90 (several signals, 8H, 2Ts). Mass spectrum: 442 (M^+; 7).

Anal. Calcd for $C_{19}H_{22}O_8S_2$: C, 51.58; H, 4.97; S, 14.47. Found: C, 51.81; H, 5.05; S, 14.59.

Compound 7: IR (KBr) 3440 (OH), 1600 (C=C, arom., Ts), 1380 (as S=O), 1200-1180 (sym S=O); ^{1}H NMR δ 2.48 (s, 3H from Ts), 2.50 (s, 3H from Ts), 2.62 (d, 1H, $J_{3,OH}$ = 5 Hz, exchangeable with D_2O, OH), 3.74 (dd, 1H, $J_{5a,4}$ = 2,1 Hz, $J_{5a,5b}$ = 11 Hz, H-5a), 4.08 (dd, 1H, $J_{5b,4}$ = 4.8 Hz, $J_{5b,5a}$ = 11 Hz, H-5b), 4.04-4.32 (tightly coupled multiplets, 3H, H-1a, H-2, H-1b), 4.43 (ddd, 1H, $J_{3,4}$ = 1.9 Hz, $J_{3,2}$ = 3.6 Hz, $J_{3,OH}$ = 5 Hz, H-3), 4.83 (ddd, 1H, $J_{4,3}$ = 1.9 Hz, $J_{4,5a}$ = 2.1 Hz, $J_{4,5b}$ = 4.8 Hz, H-4), 7.71-7.88 (several signals, 8H, 2Ts). Mass spectrum: 270 (M-TsOH; 13).

Anal. Calcd for $C_{19}H_{22}O_8S_2$: C, 51.58; H, 4.97; S, 14.47. Found: C, 51.99; H, 5.23; S, 13.91.

2,5-Anhydro-1,3,4-tri-O-p-toluenesulfonyl-D,L-xylitol (8). - A solution of xylitol (1.52 g, 10 mmol) and p-toluenesulfonyl chloride (9.5 g, 50 mmol) in dry pyridine (25 mL) was left at room temperature for 24 h. Potassium hydroxide (10 mmol) and water (5 mL) were added and the reaction mixture was stirred for additional 15 min. The reaction mixture was then poured onto ice (50 g), acidified with diluted HCl (1:1, 100 mL), and the resulting suspension was extracted with $CHCl_3$. The combined extracts were washed with water (to pH 6-7), then with saturated $NaHCO_3$ and dried (Na_2SO_4). After removal of solvent, crude

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compound 8 remained. Double recrystallization from EtOH gave an analytical sample 8 (4.52 g, 75%): mp 109 °C (lit.[18] mp 106 °C); IR (KBr) 1600 (C=C, arom.), 1370 (as S=O), 1190-1170 (sym S=O); ^{1}H NMR δ 2.55 (3s, 9H, 3 × CH_3 from 3Ts), 3.75 (dd, 1H, $J_{5a,4}$ = 2 Hz, $J_{5a,5b}$ = 11.5 Hz, H-5a), 3.95-4.25 (m, 1H, H-2), 4.87 (dd, 1H, $J_{3,4}$ = 1.5 Hz, $J_{3,2}$ = 4 Hz, H-3), 5.05 (ddd, 1H, H-4), 7.30-7.86 (several signals, 12H from 3Ts); ^{13}C NMR δ 21.63 (CH_3 from Ts), 65.95 (C-1), 71.03 (C-5), 76.53, 80.49, 81.34 (C-2, C-3, C-4), 127.85-130.22 (C-Ar), 145.12, 145.68, 146.01 (3qC, Ts). Mass spectrum: 596 (M^+; 15).

Anal. Calcd for $C_{26}H_{28}O_{10}S_3$: C, 52.34; H, 4.69; S, 16.10. Found: C, 51.99; H, 4.45; S, 16.08.

2,5-Anhydro-1,3,4-tri-O-methanesulfonyl-D,L-xylitol (9). - A solution of xylitol (1 g, 6.5 mmol) and methanesulfonyl chloride (3.72 g, 32.5 mmol) in dry pyridine (10 mL) was left at room temperature for 7 days. Using the same work-up procedure as for compound 8, crude compound 9 was obtained as a yellow solid. On recrystallization from EtOH, white crystals of pure product 9 were obtained (5.24 g, 60%): mp 127 °C; IR(KBr) 1370 (as S=O), 1180 (sym S=O); ^{1}H NMR δ 3.09-3.19 (3s, 9H, $3CH_3$ from 3Ms), 4.09 (dd, 1H, $H_{5a,5b}$ = 11.1 Hz, $J_{5a,4}$ = 2.6 Hz, H-5a), 4.40 (dd, 1H, $J_{5b,4}$ = 5.2 Hz, H-5b), 4.41-4.55 (several signals, 3H, H-1a, H-1b, H-2), 5.28 (dd, 1H, $J_{3,2}$ = 3.5 Hz, $J_{3,4}$ = 1.5 Hz, H-3), 5.32 (ddd, 1H, $J_{4,3}$ = 1.8 Hz, $J_{4,5a}$ = 2.5 Hz, $J_{4,5b}$ = 5.2 Hz, H-4); ^{13}C NMR (DMSO-d_6) δ 37.52, 37.63, 37.81, ($3CH_3$ from 3Ms), 67.23 (C-1), 70.63 (C-5), 76.55 (C-2), 80.01 (C-4), 81.71 (C-3).

Anal. Calcd for $C_8H_{16}O_{10}S_3$: C, 26.08; H, 4.34; S, 26.08. Found: C, 25.50; H, 4.40; S, 25.38.

2,5-Anhydro-4-O-benzoyl-1,3-di-O-p-toluenesulfonyl-D,L-xylitol (4'). - A solution of compound 6 (0.54 g, 1.22 mmol) and benzoyl chloride (0.24 g, 1.73 mmol) in dry pyridine (10 mL) was left at room temperature for 24 h. Under analogous experimental conditions as described in the procedure for obtaining compound

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4, crude product 4' was obtained as a solid. Crystallization from MeOH gave the pure product 4' (0.46 g, 70%): mp 96 °C; IR (KBr) 1730 (C=O); ^{1}H NMR δ 2.41 (s, 3H, CH_3 from Ts), 2.44 (s, 3H, CH_3 from Ts); 3.81 (dd, $J_{5a,4}$ = 2 Hz, $J_{5a,5b}$ = 10 Hz, 4.11-4.38 (several signals, 4H, H-2, H-5b, 2H-1), 5.04 (dd, 1H, $J_{3,4}$ = 1.5 Hz, $J_{3,2}$ = 3.5 Hz, H-3), 5.49 (ddd, 1H, $J_{4,5a}$ = 2 Hz, $J_{4,3}$ = 1.5 Hz, $J_{4,5b}$ = 3 Hz, H-4), 7.30-7.98 (several signals, 13H, arom. protons from Bz and 2Ts).

Anal. Calcd for $C_{26}H_{26}O_9S_2 \times CH_3OH$: C, 56.05; H, 5.19; S, 11.07. Found: C, 56.28; H, 4.80; S, 11.42.

2,5-Anhydro-3-O-benzoyl-1,4-di-O-p-toluenesulfonyl-D,L-xylitol (10). - A solution of compound 7 (0.57 g, 1.28 mmol) and benzoyl chloride (0.24 g, 1.73 mmol) in dry pyridine (10 mL) was left at room temperature for 24 h. Using the same work-up procedure as for compound 4, crude product 10 was obtained as a solid. On recrystallization from MeOH, white crystals of pure compound 10 were obtained (0.45 g, 64%), mp 92 °C; IR (KBr) 1730 (C=O); ^{1}H NMR δ 2.34 (s, 3H, CH_3 from Ts), 2.40 (s, 3H, CH_3 from Ts), 3.89 (dd, 1H, $J_{5a,5b}$ = 12.2 Hz, $J_{5a,4}$ = 3 Hz, H-5a), 4.12-4.18 (several signals, 2H, 2H-1), 4.23-4.47 (several signals, 2H, H-2, H-5b), 4.49-5.10 (m, 1H, H-4), 5.41-5.48 (dd, 1H, $J_{3,4}$ = 2,4 Hz, $J_{3,2}$ = 4.8 Hz, H-3), 7.13-7.87 (several signals, 13H, arom. protons from Bz and 2Ts).

Anal. Calcd for $C_{26}H_{26}O_9S_2 \times CH_3OH$: C, 56.05; H, 5.19;.S, 11.07. Found: C, 56.14; H, 4.95; S, 10.56.

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REFERENCES

1. F. J. Pilgrim, A. E. Axelrad, T. Winnick, and K. Hofmann, Science, 102, 35 (1945).

2. G. Grob, and F. Reber, Helv. Chim. Acta, 33, 1776 (1950).

3. M. Utter, and D. Keech, J. Biol. Chem., 235, PC 17 (1960).

4. K. Hoffmann, and T. Winnick, J. Biol. Chem., 160, 449 (1945).

5. D. Miljković, V. Popsavin, and J. Hranisavljević, Bull. Soc. Chim. Beograd, 48, 211 (1983).

6. D. Miljković, V. Popsavin, and B. Slavica, Ibid., 48, 219 (1983).

7. D. Miljković, V. Popsavin, and J. Harangi, Tetrahedron Lett., 28, 5733 (1987).

8. J. F. Carson, and W.D. Maclay, J. Am. Chem. Soc., 67, 1808 (1945).

9. F. Grandel, U. S. Pat., 2,375,915 (1945); Chem. Abstr., 40, 89 (1946).

10. L. F. Wiggins, Advan. Carbohydr. Chem., 5, 191 (1950).

11. S. N. Danilov, and V. F. Kazimirova, Sb. Statei Obshch. Khim., 2, 1646 (1953); Chem. Abstr., 49, 6840 (1955).

12. D. L. MacDonald, J. D. Crum, and R. Barker, J. Am. Chem. Soc., 80, 3379 (1958).

13. G. R. Gray, F. C. Hartman, and R. Barker, J. Org. Chem., 30, 2020 (1965).

14. B. G. Hudson, and R. Barker, J. Org. Chem., 32, 3650 (1967).

15. S. Soltzberg, Advan. Carbohydr. Chem., 25, 229 (1970).

16. A. Wisnievski, Carbohydr. Res., 97, 229 (1981).

17. A. Wisnievski, J. Gadjus, J. Sokolovski, and J. Szafranek, Carbohydr. Res., 114, 11 (1983).

18. S. N. Danilov, A. N. Anikeeva, and N. S. Tikhomirova-Sidorova, Zh. Obshch. Khim., 27, 2434 (1957).

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