J. Serb. Chem. Soc. 71 (7) 705–711 (2006) JSCS – 3464 UDC 547–311+546.273'161:542.9 Original scientific paper

Reactions of α-4(20)-epoxy-5-O-mesyltriacetyltaxicine I induced by BF₃·Et₂O/Bu₄NBr

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(Received 19 August 2005)

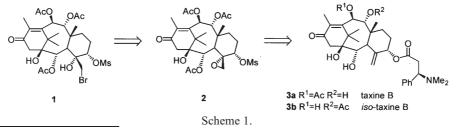
Abstract: The reaction of α -4(20)-epoxy-5-*O*-mesyltriacetyltaxicine I (2) with BF₃:Et₂O/Bu₄NBr can give rise to 4 different products. Each of these products can be obtained selectively, under the appropriate reaction conditions.

Keywords: taxoids, epoxides, rearrangement, boron trifluoride.

INTRODUCTION

As a part of our ongoing research on modified taxol analogs,¹ we required the bromohydrin 1 - a compound which possesses a good leaving group at the C-20 position of the taxane skeleton (Scheme 1).

It was planned to obtain compound 1 from the corresponding epoxide 2 by the previously reported nucleophilic opening of the 4(20)-epoxy-taxoids induced by a Lewis acid, such as BF₃·Et₂O (Scheme 1).² However, it was found that the course of this reaction is highly dependent on the reaction conditions: the opening of the epoxide ring can be followed, or preceeded, by the rearrangement of the A-ring, which can give rise to four different products. It was found that each of them could be obtained selectively, under the appropriate reaction conditions.



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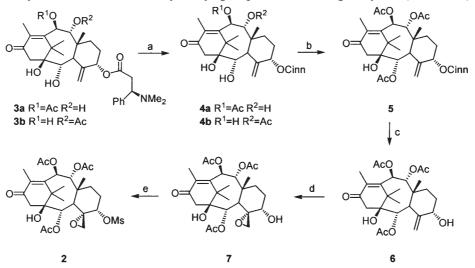
Serbian Chemical Society active member.

doi: 10.2298/JSC0607705F

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RESULTS AND DISCUSSION

Epoxide 2 was synthesized from a taxine mixture 3, obtained by simple extraction of dried leaves of the European yew *Taxus baccata*.³ Thus, treatment of crude 3 with mCPBA in THF furnished a mixture of 9- and 10-*O*-acetyl-5-*O*-cinnamoyltaxicines I 4, which was acetylated to 5-*O*-cinnamoyltaxicine I 5.⁴ Conversion of 5 to the α -4(20)-epoxy-5-hydroxytriacetyltaxicine I 7 was realized as previously described:⁵ hydrolysis of cinnamoyl moiety in 5 yielded the allylic alcohol 6, and stereoselective epoxidation of the double bond gave 7. Finally, mesylation of the free C-5 hydroxyl group afforded 2 in good yield (Scheme 2).



Reagents and conditions: a) mCPBA, THF, r.t., 48 h, 37%; b) Ac₂O, DMAP, pyridine, CH_2Cl_2 , r.t., 10 h, 80%; c) $NH_2OH \cdot HCI$, EtOH, H_2O , 80 °C, 24 h, 50%; d) mCPBA, CH_2Cl_2 , r.t, 2 h, 83%; e) MsCI, pyridine, r.t., 2 h, 90%.

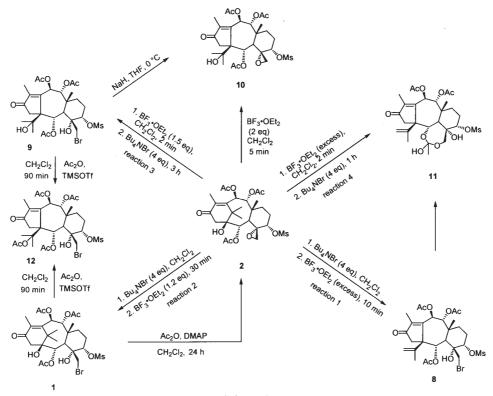
Scheme 2.

The results of our study of $BF_3 \cdot Et_2O/Bu_4NBr$ induced reactions of epoxide **2** are displayed in Scheme 3.

When a solution of **2** and Bu₄NBr (4 eq) in dry CH₂Cl₂ was treated with a large excess of BF₃·Et₂O (15 eq), compound **8** was obtained in a moderate yield (48 %) (reaction 1). Obviously, in addition to epoxide ring opening, the Lewis acid caused a contraction of the taxoid A-ring followed by the formation of a $\Delta^{15,16}$ double bond. This rearrangement has often been observed in taxoids with a free C-1 hydroxyl group, under acidic conditions.⁶ In order to avoid this rearrangement and to stop the reaction at the stage of bromohydrin **1**, the amount of the Lewis acid was diminished; indeed performing the reaction with 1.2 eq of BF₃·Et₂O allowed the desired bromohydrin **1** to be selectively obtained in 72 % yield.

It is interesting to note that the reaction course depends also on the order of the reagent addition. Thus, reversing the order of addition (*i.e.*, adding first BF_3 ·Et₂O (1.5

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Scheme 3.

eq) to a solution of **2** in CH_2Cl_2 , followed by the addition of Bu_4NBr (4 eq)), resulted in the selective conversion of epoxide **2** into compound **9** (66 % yield). In this case, the contraction of the A-ring occurred upon addition of $BF_3 \cdot Et_2O$, prior to the addition of the nucleophile. This hypothesis was confirmed by treatment of **2** with $BF_3 \cdot Et_2O$ (2 eq) in CH_2Cl_2 for 5 min; after standard work-up, the epoxide **10** was isolated in 78 % yield. Epoxide **10** was also obtained when **9** was treated with NaH in THF at 0 °C.

Finally, treatment of a solution of **2** in CH_2Cl_2 with a large excess of Lewis acid, followed by Bu_4NBr (4 eq), furnished the hemiorthoester **11** as the sole product in a moderate yield (56 %). Formation of **11** can be explained by the nucle-ophilic attack of the oxygen of the C-2 acetyl group onto the C-20 carbon. Probably, rearrangement of the A-ring induces a conformational change in the taxane skeleton, which renders the C-2 acetate to be favorably oriented for nucleophilic attack onto the C-20 carbon, bearing a good leaving group. Consistent with this hypothesis, prolonged reaction times in reaction 1 lead to the intramolecular displacement of the bromide in **8** and the formation of **11**.⁷

In order to acetylate the C-4 tertiary hydroxyl group, **1** was submitted to Ac_2O (10 eq) and DMAP (15 eq) in CH₂Cl₂ at room temperature for 24 h. Surprisingly, epoxide-ring closure occurred, which gave compound **2** in 60 % yield. An attempt

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to perform this reaction with Ac_2O in the presence of TMSOTf as a catalyst was unsuccessful,⁸ as the rearranged product **12** was isolated in 61 % yield. Unfortunately, even a catalytic amount of TMSOTf (0.3 eq) induced A-ring contraction, along with acetylation of the tertiary alcohol. Compound **12** could also be obtained by treatment of **9** with Ac_2O and TMSOTf (59 %). Interestingly, the C-4 hydroxyl group remained intact in both cases, despite the strong acylating power of the Ac_2O /TMSOTf reagent.

To summarize: the reaction of epoxide 2 with $BF_3 \cdot Et_2O/Bu_4NBr$ involves a combination of epoxide ring opening and acid-catalysed rearrangement of the A-ring. Depending on the stoichiometry of the reaction, the order of the reagent addition and the reaction time, 4 different products can be formed. Under appropriate conditions, each of these products can be obtained selectively.

EXPERIMENTAL

Standard techniques were used for the purification of reagents and solvents. NMR spectra were recorded on a Varian Gemini 200 instrument, ¹H-NMR at 200 MHz, ¹³C-NMR at 50 MHz, for samples in deuterated chloroform. Chemical shifts are expressed in ppm using tetramethylsilane as the internal standard, coupling constants (*J*) are in Hz. IR spectra were recorded on a Perkin-Elmer 457 grating FT instrument, and are expressed in cm⁻¹. Mass spectra were obtained on a Finnigan ITDS 700 instrument. All chromatographic separations were performed on Silica, 10-18, 60A, ICN Biomedicals.

Compounds **4a** and **4b**: To a solution of **3a** and **3b** (5.0 g) in THF (25 mL) was added mCPBA (1.75 g) and the reaction mixture was stirred for 48 h at rt. The mixture was diluted with CH_2Cl_2 , washed successively with aq. NaHCO₃ and water, dried over anh. MgSO₄, and the solvent was removed under reduced pressure. Purification by dry-flash chromatography (eluent: benzene/ethyl acetate = 8/2) afforded a mixture of **4a** and **4b** (1.68 g) as a white foam. The ¹H and ¹³C NMR spectra of compounds **4a** and **4b** were identical to those previously reported.^{4c}

Compound 5: A mixture of 4a and 4b (220 mg) was dissolved in CH_2Cl_2 (45 mL) and treated with acetic anhydride (250 mg), pyridine (96 mg) and DMAP (5 mg). The reaction mixture was stirred at rt for 24 h and then diluted with CH_2Cl_2 , washed with 1.5 M HCl and water, dried over anhydrous MgSO₄ and the solvent evaporated under reduced pressure. Purification of the residue by dry flash chromatography (eluent: benzene/ethyl acetate = 8/2) afforded 5 (200 mg; 80 %) as a colourless film. The ¹H and ¹³C NMR spectra of compound 5 were identical to those previously reported.⁴

Compound **6**: To a mixture of **5** (140 mg) and hydroxylamine hydrochloride (140 mg) in ethanol (14 mL) was added sodium acetate (340 mg) in water (14 mL) and the reaction mixture was heated at 80 °C for 24 h. After cooling to rt, reaction mixture was diluted with water and extracted with CH_2Cl_2 . The combined organic layers were dried over anh. MgSO₄ and the solvent was removed under reduced pressure. Purification of the residue by dry flash chromatography (eluent: benzene/ethyl acetate = 7/3) afforded **6** (55 mg; 50 %) as a colourless film. The ¹H and ¹³C NMR spectra of compound **6** were identical to those previously reported.⁵

Compound 7: To a solution of **6** (160 mg) in CH_2Cl_2 (5 mL) was added mCPBA (84 mg). The reaction mixture was stirred at rt for 3 h. The mixture was diluted with CH_2Cl_2 , washed successively with aq. NaHCO₃ and water, dried over anh. MgSO₄, and the solvent was removed under reduced pressure. Purification by dry-flash chromatography (eluent: benzene/ethyl acetate = 9/1) afforded 7 (131 mg, 83 %) as a colourless film. The ¹H and ¹³C NMR spectra of compound 7 were identical to those previously reported.⁵

Compound **2**: To a solution of **7** (100 mg) in pyridine (6 mL) at 0 °C was added mesyl chloride (338 mg). The reaction mixture was stirred at 0 °C for 15 min and then for 2 h at rt. The reaction mix-

ture was diluted with CH_2Cl_2 and the resulting solution was washed successively with ice-cold 2.5 % HCl, aq. NaHCO₃ and water and dried over anh. MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by dry flash chromatography (eluent: benzene/ethyl acetate = 1/1) to give **2** (105 mg, 90 %) as a colourless film. ¹H NMR (200 MHz; CDCl₃) δ : 6.12 (1H, *d*, *J* = 10.4 Hz), 5.92 (1H, *d*, *J* = 10.2 Hz), 5.60 (1H, *d*, *J* = 4.0 Hz), 4.10 (1H, *bs*), 3.43 (1H, *d*, *J* = 3.8 Hz), 3.07 (3H, *s*), 3.04 (1H, *d*, *J* = 4.4 Hz), 3.02 (1H, *d*, *J* = 19.6 Hz), 2.67 (1H, *d*, *J* = 19.6 Hz), 2.59 (1H, *d*, *J* = 4.4 Hz), 2.29 (3H, *s*), 2.11 (3H, *s*), 2.07 (3H, *s*), 2.00 – 1.50 (4H, *m*), 1.64 (3H, *s*), 1.21 (3H, *s*), 0.98 (3H, *s*); ¹³C NMR (50 MHz, CDCl₃) δ : 198.84 (C), 171.47 (C), 169.87 (C), 169.47 (C), 152.72 (C), 142.11 (C), 87.10 (CH), 76.82 (C), 74.94 (CH), 72.61 (CH), 71.85 (CH), 60.03 (C), 51.13 (CH₂), 44.37 (C), 44.14 (CH₂), 43.50 (C), 39.91 (CH), 38.67 (CH₃), 34.07 (CH₃), 26.86 (CH₂), 25.58 (CH₂), 21.03 (CH₃), 20.78 (CH₃), 20.58 (CH₃), 19.34 (CH₃), 17.34 (CH₃), 13.93 (CH₃); IR (film) ν_{max} : 3525, 3503, 2979, 2941, 1747, 1674, 1435, 1371, 1229, 1027; MS/CI_{isobutane} 587 (M+1).

Compound **8**: To a solution of **2** (63 mg) and Bu₄NBr (138 mg) in CH₂Cl₂ (6 mL) was added BF₃·Et₂O (195 µL) dropwise at rt under an argon atmosphere. The reaction mixture was stirred for 10 min and then partitioned between CH₂Cl₂ and saturated aqueous NaHCO₃. The organic layer was separated and washed with water, dried over anh. MgSO₄ and the solvent evaporated under reduced pressure. The residue was chromatographed on silica gel (eluent: benzene/ethyl acetate = 7/3) to give **8** (33 mg, 48 %) as a colourless film. ¹H NMR (200 MHz; CDCl₃) δ : 6.15 (1H, *d*, *J* = 9.8 Hz), 6.08 (1H, *d*, *J* = 7.2 Hz), 5.31 (1H, *d*, *J* = 9.8 Hz), 5.18 (1H, *s*) 5.05 (1H, *d*, *J* = 1.2 Hz), 4.82 (1H, *m*), 3.63 (1H, *d*, *J* = 12.2 Hz), 3.38 (1H, *d*, *J* = 12.2 Hz), 3.12 (1H, *d*, *J* = 18.6 Hz), 2.06 (3H, *s*), 2.67 (1H, *d*, *J* = 7.2 Hz), 2.42 (1H, *d*, *J* = 18.4 Hz), 2.15 (3H, *s*), 2.09 – 1.50 (4H, *m*), 2.07 (3H, *s*), 1.97 (3H, *s*), 1.86 (3H, *s*), 1.55 (3H, *s*), 1.15 (3H, *s*); ¹³C NMR (50 MHz, CDCl₃) δ : 207.09 (C), 170.76 (C), 169.91 (C), 169.07 (C), 162.26 (C), 143.65 (C), 143.14 (C), 113.65 (CH₂), 80.33 (CH), 75.58 (CH), 72.08 (C), 70.03 (CH), 67.71 (CH), 60.52 (C), 46.72 (CH), 44.81 (CH₂), 40.88 (C), 38.35 (CH₃), 37.35 (CH₂), 25.37 (CH₂), 24.67 (CH₂), 21.43 (CH₃), 20.58 (CH₃), 20.43 (CH₃), 20.27 (CH₃), 18.70 (CH₃), 8.45 (CH₃); IR (film) ν_{max} : 3523, 3417, 2955, 2862, 1751, 1696, 1435, 1374, 1231, 1024; HRMS (FAB) Calcd for C₂₇H₃₇O₁₁SBrNa (M+Na⁺) 671.1154, found 671.1132.

Compound 1: To a solution of **2** (43 mg) and Bu₄NBr (95 mg) in CH₂Cl₂ (15 mL) was added BF₃·Et₂O (9.8 µL) dropwise at rt under an argon atmosphere. The reaction mixture was stirred for 30 min and then partitioned between CH₂Cl₂ and saturated aqueous NaHCO₃. The organic layer was separated and washed with water, dried over anh. MgSO₄ and the solvent evaporated under reduced pressure. The residue was chromatographed on silica gel (eluent: benzene/ethyl acetate = 1/1) to give **1** (35 mg, 72 %) as a colourless film. ¹H NMR (200 MHz; CDCl₃) δ : 6.09 (1H, *d*, *J* = 10.4 Hz), 5.81 (1H, *d*, *J* = 10.4 Hz), 5.65 (1H, *d*, *J* = 5.0 Hz), 4.82–4.80 (1H, *m*), 3.61 (1H, *d*, *J* = 11.8 Hz), 3.54 (1H, *d*, *J* = 11.8 Hz), 3.42 (1H, *d*, *J* = 19.6 Hz), 3.29 (1H, *d*, *J* = 5.0 Hz), 3.12 (1H, *s*), 3.03 (3H, *s*), 2.61 (1H, *d*, *J* = 19.4 Hz), 2.26 (3H, *s*), 2.25 (3H, *s*), 2.11 (3H, *s*), 2.10–1.60 (4H, *m*), 2.06 (3H, *s*), 1.68 (3H, *s*), 1.23 (3H, *s*), 0.90 (3H, *s*); ¹³C NMR (50 MHz, CDCl₃) δ : 198.84 (C), 171.33 (C), 170.24 (C), 169.25 (C), 151.97 (C), 141.67 (C), 80.75 (CH), 78.27 (C), 74.71 (CH), 73.58 (CH), 73.19 (C), 72.45 (CH), 47.58 (CH), 43.26 (CH₂), 43.10 (C), 42.64 (C), 38.80 (CH₂), 38.71 (CH₃), 34.38 (CH₃), 25.10 (CH₂), 24.84 (CH₂), 21.34 (CH₃), 20.80 (CH₃), 20.67 (CH₃), 19.58 (CH₃), 18.96 (CH₃), 13.37 (CH₃); IR (film) *v*_{max}: 3545, 3408, 2992, 2940, 1750, 1674, 1374, 1352, 1229, 1027; HRMS (FAB) Calcd for C₂₇H₃₉O₁₂SBrNa (M+Na⁺) 689.1235, found 689.1238.

Compound **9**: To a solution of **2** (30 mg) in CH₂Cl₂ (4 mL) was added BF₃·Et₂O (9.6 μ L) dropwise at rt under an argon atmosphere. After 2 min, Bu₄NBr (50 mg) was added and the reaction mixture was stirred at rt for 3 h. The mixture was diluted with CH₂Cl₂ and washed successively with saturated aq. NaHCO₃ and water, dried over anh. MgSO₄ and the solvent evaporated under reduced pressure. The residue was chromatographed on silica gel (eluent: benzene/ethyl acetate = 6/4) to give **9** (27 mg, 66 %) as a colourless film. ¹H NMR (200 MHz; CDCl₃) δ : 6.28 (1H, *d*, *J* = 10.4 Hz), 6.11 (1H, *d*, *J* = 7.0 Hz), 5.99 (1H, *d*, *J* = 10.4 Hz), 4.89–4.88 (1H, *m*), 3.62 (1H, *d*, *J* = 12.2 Hz), 3.88 (1H, *d*, *J* = 12.2 Hz), 3.06 (1H, *d*, *J* = 18.6 Hz), 2.93 (3H, *s*), 2.65 (1H, *d*, *J* = 7.0 Hz), 2.41 (1H, *d*, *J* =

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18.4 Hz), 2.14 (3H, *s*), 2.10–1.50 (4H, *m*), 2.06 (3H, *s*), 2.03 (3H, *s*), 1.87 (3H, *s*), 1.17 (3H, *s*), 1.12 (3H, *s*), 1.11 (3H, *s*); ¹³C NMR (50 MHz, CDCl₃) δ : 207.27 (C), 171.04 (C), 170.13 (C), 168.21 (C), 162.43 (C), 145.33 (C), 80.55 (CH), 76.23 (CH), 75.30 (C), 72.12 (C), 69.10 (CH), 68.24 (CH), 64.60 (C), 47.51 (CH), 43.64 (CH₂), 40.71 (C), 38.37 (CH₃), 37.27 (CH₂), 27.73 (CH₃), 26.17 (CH₃), 25.15 (CH₂), 24.69 (CH₂), 21.77 (CH₃), 20.54 (2 × CH₃), 18.61 (CH₃), 8.42 (CH₃); IR (film) ν_{max} : 3539, 3508, 3437, 2979, 2940, 1751, 1709, 1373, 1346, 1234, 1025; HRMS (FAB) Calcd for C₂₇H₃₉O₁₂SBrNa (M+Na⁺) 689.1235, found 689.1238.

Compound **10**: To a solution of **2** (65 mg) in CH₂Cl₂ (8 mL) was added BF₃:Et₂O (27 μ L) dropwise at rt under an argon atmosphere. The reaction mixture was stirred for 5 min and then partitioned between CH₂Cl₂ and saturated aq. NaHCO₃. The organic layer was separated and washed with water, dried over anh. MgSO₄ and the solvent evaporated under reduced pressure. The residue was chromatographed on silica gel (eluent: benzene/ethyl acetate = 1/1) to give **10** (51 mg, 78 %) as a colourless film. ¹H NMR (200 MHz; CDCl₃) δ : 6.33 (1H, *d*, *J* = 10.4 Hz), 6.06 (1H, *d*, *J* = 10.4 Hz), 5.98 (1H, *d*, *J* = 8.2 Hz), 4.12 (1H, *m*), 2.99 (3H, *s*), 2.96 (1H, *d*, *J* = 3.6 Hz), 2.78 (1H, *d*, *J* = 19.2 Hz), 2.75 (1H, *d*, *J* = 8.4 Hz), 2.60 (1H, *d*, *J* = 3.6 Hz), 2.54 (1H, *s*), 2.40 (1H, *d*, *J* = 19.2 Hz), 2.10–1.50 (4H, *m*), 2.07 (3H, *s*), 2.04 (3H, *s*), 2.01 (3H, *s*), 1.93 (3H, *s*), 1.18 (3H, *s*), 1.14 (3H, *s*), 1.05 (3H, *s*); ¹³C NMR (50 MHz, CDCl₃) δ ; 206.91 (C), 171.53 (C), 169.92 (C), 169.18 (C), 161.48 (C), 146.47 (C), 86.35 (CH), 75.72 (CH), 75.25 (C), 68.23 (CH), 67.52 (CH), 64.47 (C), 59.82 (C), 50.36 (CH₂), 43.68 (CH₂), 42.66 (C), 39.65 (CH), 38.69 (CH₃), 27.41 (CH₃), 27.12 (CH₂), 26.17 (CH₃), 26.00 (CH₂), 21.67 (CH₃), 20.60 (CH₃), 16.98 (CH₃), 8.55 (CH₃); MS/Cl_{isobutane} 587 (M+1).

Compound 11: To a solution of 2 (23 mg) in CH₂Cl₂ (2.5 mL) was added BF₃·Et₂O (75 µL) dropwise at rt under an argon atmosphere. After 2 min, Bu₄NBr (51 mg) was added and the reaction mixture was stirred at rt for 1 h. The mixture was diluted with CH₂Cl₂ and washed successively with saturated aq. NaHCO₃ and water, dried over anh. MgSO₄ and the solvent evaporated under reduced pressure. The residue was chromatographed on silica gel (eluent: benzene/ethyl acetate = 7/3) to give 11 (13 mg, 58 %) as a colourless film. ¹H NMR (200 MHz; CDCl₃) δ : 5.96 (1H, d, J = 4.6 Hz), 4.98 (1H, *bs*), 4.95 (1H, *bs*), 4.87 (1H, *d*, *J* = 4.6 Hz), 4.85 (1H, *bs*), 4.79 (1H, *d*, *J* = 7.7 Hz), 3.97 (1H, *d*, *J* = 9.0 Hz), 3.77 (1H, *d*, *J* = 9.0 Hz), 3.08 (3H, *s*), 2.62 (1H, *d*, *J* = 18.9 Hz), 2.37 (1H, *d*, *J* = 18.9 Hz), 2.09 (3H, s), 2.01 (3H, s), 2.00–1.50 (4H, m), 1.89 (1H, d, J = 4.0 Hz), 1.83 (3H, s), 1.67 (3H, *s*), 1.58 (3H, *s*), 1.51 (3H, *s*); ¹³C NMR (50 MHz, CDCl₃) δ: 207.39 (C), 169.29 (C), 168.98 (C), 162.11 (C), 146.38 (C), 142.98 (C), 121.42 (C), 111.96 (CH₂), 80.40 (CH), 77.73 (C), 77.25 (CH), 73.90 (CH₂), 70.34 (2 × CH), 55.97 (C), 44.57 (CH₂), 43.12 (CH), 40.50 (C), 39.20 (CH₃), 28.21 (CH₂), 22.74 (CH₂), 20.89 (CH₃), 20.61 (CH₃), 20.50 (CH₃), 20.45 (CH₃), 20.14 (CH₃), 9.14 (CH₃); IR (film v_{max}: 3464, 3409, 2943, 1750, 1710, 1640, 1445, 1404, 1369, 1303, 1225, 1174, 1113, 1047, 1028; HRMS (MALDI TOF) Calcd for C₂₇H₃₇O₁₁S⁺ (MH⁺–H₂O) 569.2051, found 569.1730.

Compound **12**: A solution of **1** (35 mg) in CH₂Cl₂ (4 mL) was treated with Ac₂O (22 mg) at rt, followed by a solution of TMSOTf (3.5 mg) in CH₂Cl₂. The reaction mixture was stirred for 1.5 h at rt. The reaction was quenched with methanol, diluted with CH₂Cl₂, and washed with NaHCO₃ and water. The organic phase was dried over anh. MgSO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: benzene/ethyl acetate = 7/3) to give **12** (22 mg, 61 %) as a colourless film. ¹H NMR (200 MHz; CDCl₃) δ : 6.27 (1H, *d*, *J* = 10.2 Hz), 6.17 (1H, *d*, *J* = 6.6 Hz), 5.70 (1H, *d*, *J* = 10.2 Hz), 4.89–4.87 (1H, *m*), 3.63 (1H, *d*, *J* = 12.0 Hz), 3.32 (1H, *d*, *J* = 11.8 Hz), 3.24 (1H, *d*, *J* = 18.8 Hz), 2.98 (1H, *s*), 2.93 (3H, *s*), 2.68 (1H, *d*, *J* = 6.6 Hz), 5.13 (3H, *s*), 1.38 (3H, *s*), 1.13 (3H, *s*); ¹³C NMR (50 MHz, CDCl₃) δ : 206.92 (C), 170.96 (C), 170.42 (C), 170.11 (C), 168.96 (C), 161.79 (C), 146.68 (C), 85.37 (C), 80.35 (CH), 77.64 (CH), 72.10 (C), 68.35 (CH), 68.19 (CH), 64.40 (C), 47.14 (CH), 42.19 (CH₂), 41.21 (C), 38.42 (CH₃), 37.25 (CH₂), 25.55 (CH₂), 24.71 (CH₂), 23.62 (C), 23.04 (CH₃), 22.73 (CH₃), 21.83 (CH₃), 20.67 (CH₃), 20.52 (CH₃), 19.05 (CH₃), 8.60 (CH₃).

ИЗВОД

РЕАКЦИЈЕ α-4(20)-ЕПОКСИ-5-*О*-МЕЗИЛТРИАЦЕТИЛТАКСИЦИНА I СА ТЕТРАБУТИЛАМОНИЈУМ-БРОМИДОМ У ПРИСУСТВУ БОРТРИФЛУОРИД-ЕТЕРАТА

зорана ферјанчић $^{1,2},$ радомир матовић 2 живорад чековић 2 и радомир н. саичић 1,2

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У реакцији α -4(20)-епокси-5-*O*-мезилтриацетилтаксицина I (**2**) са бортрифлуорид-етератом и тетрабутиламонијум-бромидом могу настати 4 различита производа, у зависности од реакционих услова. Сваки од ова 4 производа се може добити селективно, под одговарајућим реакционим условима.

(Примљено 19. августа 2005)

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