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Reactions of α-4(20)-epoxy-5-*O*-mesyltriacetyltaxicine I induced by $BF_3{\cdot}Et_2O/Bu_4NBr$

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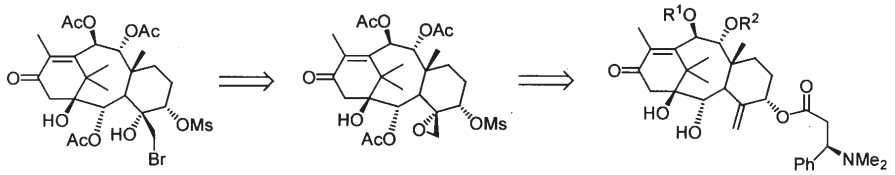
Abstract: The reaction of α-4(20)-epoxy-5-*O*-mesyltriacetyltaxicine I (**2**) with $BF_3{\cdot}Et_2O/Bu_4NBr$ can give rise to 4 different products. Each of these products can be obtained selectively, under the appropriate reaction conditions.

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 $BF_3{\cdot}Et_2O$ (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.



Scheme 1.

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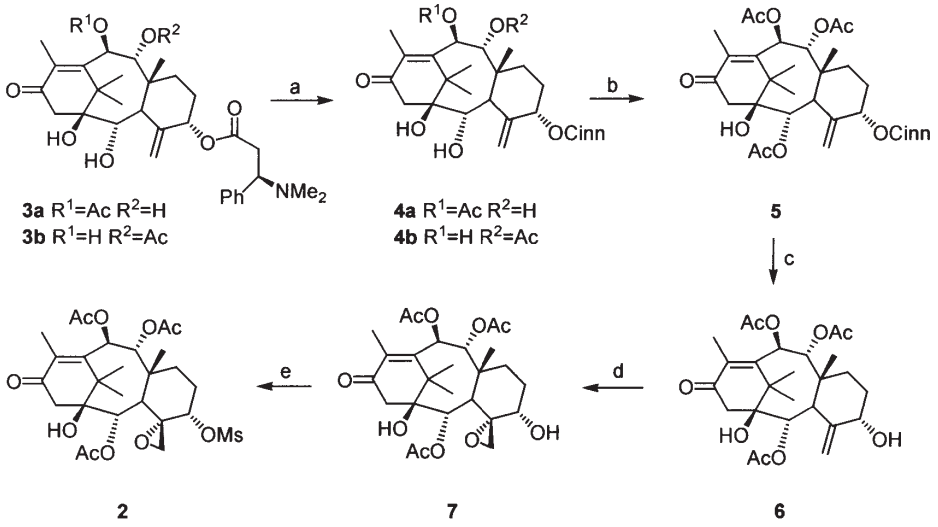
RESULTS AND DISCUSSION

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).



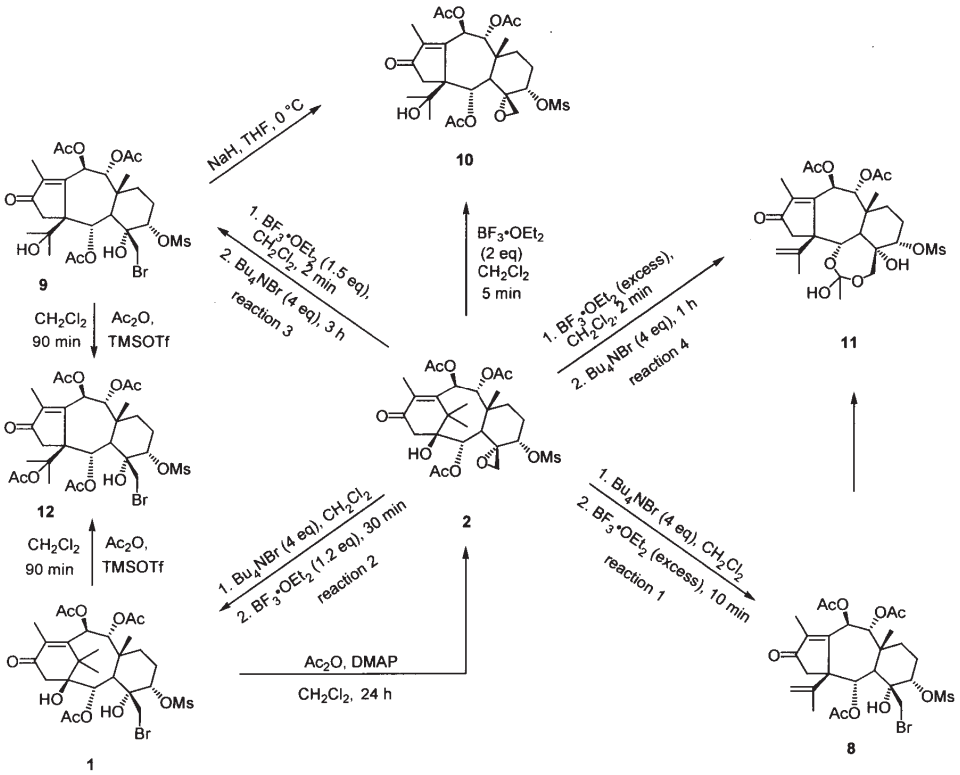
Reagents and conditions: a) mCPBA, THF, r.t., 48 h, 37%; b) Ac_2O, DMAP, pyridine, CH_2Cl_2, r.t., 10 h, 80%; c) NH_2OH •HCl, EtOH, H_2O, 80 °C, 24 h, 50%; d) mCPBA, CH_2Cl_2, r.t, 2 h, 83%; e) MsCl, pyridine, r.t., 2 h, 90%.

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 Bu_4NBr (4 eq) in dry CH_2Cl_2 was treated with a large excess of $BF_3{\cdot}Et_2O$ (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 $BF_3{\cdot}Et_2O$ 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 $BF_3{\cdot}Et_2O$ (1.5



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 ºC.

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 nucleophilic 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 CH_2Cl_2 at room temperature for 24 h. Surprisingly, epoxide-ring closure occurred, which gave compound **2** in 60 % yield. An attempt

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, ^{1}H-NMR at 200 MHz, ^{13}C-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. $NaHCO_3$ and water, dried over anh. $MgSO_4$, 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 ^{1}H and ^{13}C 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 $MgSO_4$ 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 ^{1}H and ^{13}C 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 ºC 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. $MgSO_4$ 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 ^{1}H and ^{13}C 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. $NaHCO_3$ and water, dried over anh. $MgSO_4$, 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 ^{1}H and ^{13}C 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 ºC was added mesyl chloride (338 mg). The reaction mixture was stirred at 0 ºC 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. $NaHCO_3$ and water and dried over anh. $MgSO_4$. 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. ^{1}H NMR (200 MHz; $CDCl_3$) 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*), 2.14 (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*); ^{13}C NMR (50 MHz, $CDCl_3$) 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 (CH_2), 44.37 (C), 44.14 (CH_2), 43.50 (C), 39.91 (CH), 38.67 (CH_3), 34.07 (CH_3), 26.86 (CH_2), 25.58 (CH_2), 21.03 (CH_3), 20.78 (CH_3), 20.58 (CH_3), 19.34 (CH_3), 17.34 (CH_3), 13.93 (CH_3); 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 Bu_4NBr (138 mg) in CH_2Cl_2 (6 mL) was added $BF_3{\cdot}Et_2O$ (195 μL) dropwise at rt under an argon atmosphere. The reaction mixture was stirred for 10 min and then partitioned between CH_2Cl_2 and saturated aqueous $NaHCO_3$. The organic layer was separated and washed with water, dried over anh. $MgSO_4$ 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. ^{1}H NMR (200 MHz; $CDCl_3$) 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), 2.96 (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*); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 207.09 (C), 170.76 (C), 169.91 (C), 169.07 (C), 162.26 (C), 143.65 (C), 143.14 (C), 113.65 (CH_2), 80.33 (CH), 75.58 (CH), 72.08 (C), 70.03 (CH), 67.71 (CH), 60.52 (C), 46.72 (CH), 44.81 (CH_2), 40.88 (C), 38.35 (CH_3), 37.35 (CH_2), 25.37 (CH_2), 24.67 (CH_2), 21.43 (CH_3), 20.58 (CH_3), 20.43 (CH_3), 20.27 (CH_3), 18.70 (CH_3), 8.45 (CH_3); IR (film) ν_{max}: 3523, 3417, 2955, 2862, 1751, 1696, 1435, 1374, 1231, 1024; HRMS (FAB) Calcd for $C_{27}H_{37}O_{11}SBrNa$ (M+Na^+) 671.1154, found 671.1132.

Compound **1**: To a solution of **2** (43 mg) and Bu_4NBr (95 mg) in CH_2Cl_2 (15 mL) was added $BF_3{\cdot}Et_2O$ (9.8 μL) dropwise at rt under an argon atmosphere. The reaction mixture was stirred for 30 min and then partitioned between CH_2Cl_2 and saturated aqueous $NaHCO_3$. The organic layer was separated and washed with water, dried over anh. $MgSO_4$ 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. ^{1}H NMR (200 MHz; $CDCl_3$) 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*); ^{13}C NMR (50 MHz, $CDCl_3$) 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 (CH_2), 43.10 (C), 42.64 (C), 38.80 (CH_2), 38.71 (CH_3), 34.38 (CH_3), 25.10 (CH_2), 24.84 (CH_2), 21.34 (CH_3), 20.80 (CH_3), 20.67 (CH_3), 19.58 (CH_3), 18.96 (CH_3), 13.37 (CH_3); IR (film) ν_{max}: 3545, 3408, 2992, 2940, 1750, 1674, 1374, 1352, 1229, 1027; HRMS (FAB) Calcd for $C_{27}H_{39}O_{12}SBrNa$ (M+Na^+) 689.1235, found 689.1238.

Compound **9**: To a solution of **2** (30 mg) in CH_2Cl_2 (4 mL) was added $BF_3{\cdot}Et_2O$ (9.6 μL) dropwise at rt under an argon atmosphere. After 2 min, Bu_4NBr (50 mg) was added and the reaction mixture was stirred at rt for 3 h. The mixture was diluted with CH_2Cl_2 and washed successively with saturated aq. $NaHCO_3$ and water, dried over anh. $MgSO_4$ 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. ^{1}H NMR (200 MHz; $CDCl_3$) 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), 3.38 (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* =

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*); ^{13}C NMR (50 MHz, $CDCl_3$) 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 (CH_2), 40.71 (C), 38.37 (CH_3), 37.27 (CH_2), 27.73 (CH_3), 26.17 (CH_3), 25.15 (CH_2), 24.69 (CH_2), 21.77 (CH_3), 20.54 (2 × CH_3), 18.61 (CH_3), 8.42 (CH_3); IR (film) ν_{max}: 3539, 3508, 3437, 2979, 2940, 1751, 1709, 1373, 1346, 1234, 1025; HRMS (FAB) Calcd for $C_{27}H_{39}O_{12}SBrNa$ ($M+Na^+$) 689.1235, found 689.1238.

Compound **10**: To a solution of **2** (65 mg) in CH_2Cl_2 (8 mL) was added $BF_3{\cdot}Et_2O$ (27 μL) dropwise at rt under an argon atmosphere. The reaction mixture was stirred for 5 min and then partitioned between CH_2Cl_2 and saturated aq. $NaHCO_3$. The organic layer was separated and washed with water, dried over anh. $MgSO_4$ 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. ^{1}H NMR (200 MHz; $CDCl_3$) 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*); ^{13}C NMR (50 MHz, $CDCl_3$) 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 (CH_2), 43.68 (CH_2), 42.66 (C), 39.65 (CH), 38.69 (CH_3), 27.41 (CH_3), 27.12 (CH_2), 26.17 (CH_3), 26.00 (CH_2), 21.67 (CH_3), 20.60 (CH_3), 16.98 (CH_3), 8.55 (CH_3); $MS/CI_{isobutane}$ 587 (M+1).

Compound **11**: To a solution of **2** (23 mg) in CH_2Cl_2 (2.5 mL) was added $BF_3{\cdot}Et_2O$ (75 μL) dropwise at rt under an argon atmosphere. After 2 min, Bu_4NBr (51 mg) was added and the reaction mixture was stirred at rt for 1 h. The mixture was diluted with CH_2Cl_2 and washed successively with saturated aq. $NaHCO_3$ and water, dried over anh. $MgSO_4$ 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. ^{1}H NMR (200 MHz; $CDCl_3$) 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*); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 207.39 (C), 169.29 (C), 168.98 (C), 162.11 (C), 146.38 (C), 142.98 (C), 121.42 (C), 111.96 (CH_2), 80.40 (CH), 77.73 (C), 77.25 (CH), 73.90 (CH_2), 70.34 (2 × CH), 55.97 (C), 44.57 (CH_2), 43.12 (CH), 40.50 (C), 39.20 (CH_3), 28.21 (CH_2), 22.74 (CH_2), 20.89 (CH_3), 20.61 (CH_3), 20.50 (CH_3), 20.45 (CH_3), 20.14 (CH_3), 9.14 (CH_3); IR (film ν_{max}: 3464, 3409, 2943, 1750, 1710, 1640, 1445, 1404, 1369, 1303, 1225, 1174, 1113, 1047, 1028; HRMS (MALDI TOF) Calcd for $C_{27}H_{37}O_{11}S^+$ ($MH^+–H_2O$) 569.2051, found 569.1730.

Compound **12**: A solution of **1** (35 mg) in CH_2Cl_2 (4 mL) was treated with Ac_2O (22 mg) at rt, followed by a solution of TMSOTf (3.5 mg) in CH_2Cl_2. The reaction mixture was stirred for 1.5 h at rt. The reaction was quenched with methanol, diluted with CH_2Cl_2, and washed with $NaHCO_3$ and water. The organic phase was dried over anh. $MgSO_4$ 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. ^{1}H NMR (200 MHz; $CDCl_3$) 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), 2.47 (1H, *d*, *J* = 18.8 Hz), 2.21 (3H, *s*), 2.16 (3H, *s*), 2.10–1.50 (4H, *m*), 2.07 (3H, *s*), 1.98 (3H, *s*), 1.92 (3H, *s*), 1.53 (3H, *s*), 1.38 (3H, *s*), 1.13 (3H, *s*); ^{13}C NMR (50 MHz, $CDCl_3$) 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 (CH_2), 41.21 (C), 38.42 (CH_3), 37.25 (CH_2), 25.55 (CH_2), 24.71 (CH_2), 23.62 (C), 23.04 (CH_3), 22.73 (CH_3), 21.83 (CH_3), 20.67 (CH_3), 20.52 (CH_3), 19.05 (CH_3), 8.60 (CH_3).

ИЗВОД

РЕАКЦИЈЕ α-4(20)-ЕПОКСИ-5-*O*-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.

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