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Stereochemical Course of [2+2]Cycloaddition of Chlorosulfonyl Isocyanate to *cis* and *trans* 3-*O*-But-1'-enyl-1,2-*O*-isopropylidene-α-D-xylofuranose

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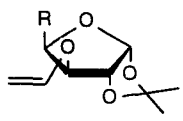
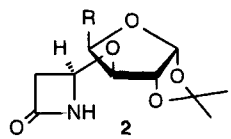
Abstract. The asymmetric [2+2]cycloaddition of chlorosulfonyl isocyanate to Z and E 3-*O*-butyl-1'-enyl-1,2-*O*-isopropylidene-5-*O*-trityl-α-D-xylofuranoses proceeds with excellent stereoselectivity affording *cis* azetidinone **12** from *cis* olefin and *trans* azetidine **13** from *trans* olefin, whereas in both cases R configuration is induced at C-4' of the azetidin-2-one ring. Intramolecular cyclization of azetidinones **16** and **17** affords respective diasteromeric cephams **18** and **19**.

Recently we have reported that the asymmetric [2+2]cycloaddition of chlorosulfonyl isocyanate to 1,2-*O*-isopropylidene-3-*O*-vinyl-glycofuranoses **1** afforded excellent stereoselectivity if a bulky R substituent at the C-4 carbon atom is present providing the (4'R) substituent of azetidinone **2**.[1] Cycloadditions have been performed in the presence of anhydrous sodium carbonate as an agent neutralizing acidic contaminations present in the commercially available reagent.[2] High asymmetric induction stimulated us to investigate the stereochemical outcome of the cycloaddition to *cis* and *trans* 3-*O*-but-1-enyl derivatives **3** and **4** with the aim of examining the reaction model proposed by us for simple 3-*O*-vinyl compound **1**. Additionally, the substrates **3** and **4** would eventually provide 1-oxacepham skeletons having 7-ethyl substituent which is present in certain active β-lactam antibiotics (for example, the carbapenem antibiotic PS-5).[3]



1



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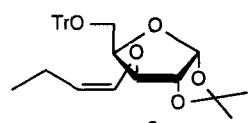

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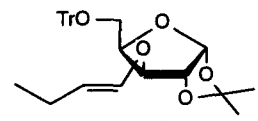
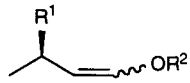


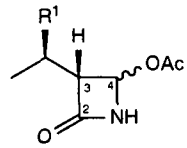
4

[2+2]Cycloaddition of tosyl isocyanate to *cis* and *trans* but-1-enyl ethers has been studied by Effenberger's group[4] in detail. Concerted formation of the four-membered β-lactam ring and a stepwise reaction proceeding *via* a zwitterionic intermediate for epimerization at C-4 or for rearrangement to the α,β-unsaturated amide have been proposed. The mechanistic proposition was based on the specificity of the reaction which transformed *cis* vinyl ethers into *cis* 3,4-disubstituted azetidinones and *trans* vinyl ethers into *trans* adducts.[4] This opinion has recently been supported by *ab initio* calculations which predicted a concerted mechanism involving retention of configuration of the starting olefin.[5] The same stereospecificity has been reported for [2+2]cycloaddition of chlorosulfonyl isocyanate to *cis* and *trans* propenyl acetates.[6]

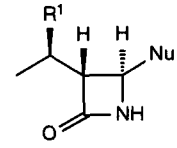
[2+2]Cycloaddition of chlorosulfonyl isocyanate to vinyl esters **5** is known to be the easiest access to 3-substituted-4-acetoxy-azetidin-2-ones **6.** It is known that **6** is a very useful starting material for the synthesis of β-lactam antibiotics because the acetoxy group can be replaced by a variety of nucleophiles.[6]



5: R^1= H, CH_3, OSi *t*- $BuMe_2$
R^2= Acyl, TMS



6



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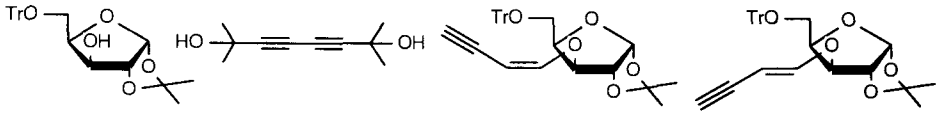
The configuration of the double bond in **5** does not influence the face-differentiation of the [2+2]cycloaddition and consequently, from both geometric isomers the same configuration at C-3 of the azetidinone **6** was induced. Owing to the flat intermediate, nucleophilic substitution of the acetoxy group in both *cis* and *trans* 3-substituted-4-acetoxyazetidin-2-ones **6** provide the same 3,4-*trans* product **7**. Our approach to 1-oxabicyclic-β-lactams from vinyl ether type compounds anticipate further transformation of the 4-alkoxy group into the second ring of antibiotic, therefore the control of the absolute configuration of both C-3 and C-4 carbon atoms of the azetidin-2-one is essential. One could expect that the steric course of the [2+2]cycloaddition would be the same as that found by Effenberger[4] for tosyl isocyanate and simple vinyl ethers, but the (4'R) configuration of the azetidin-2-one fragment would be induced.

Compounds **3** and **4** were obtained from the readily available sugar **8**.[7] Treatment of **8** with diacetylene glycol **9** according to the David et al. procedure[8] afforded a mixture of *cis* and *trans* olefins **10** and **11** in a ratio 3:7, respectively. The mixture was separated by chromatography into pure components. Hydrogenation of the triple bond in **10** and **11** over $Pd/BaSO_4$ catalyst gave **3** and **4**, respectively in excellent yield.

[2+2]Cycloaddition of chlorosulfonyl isocyanate to vinyl ethers **3** and **4** in the presence of sodium carbonate followed by reduction of the *N*-chlorosulfonyl substituent with Red-Al[9] provided azetidinones **12**

and **13**, respectively - as single diastereomers in 75-80 % yield. The *cis* olefin **3** afforded *cis* 3,4-disubstituted azetidin-2-one **12** whereas the *trans* olefin **4** gave the *trans* compound **13**. Detritylation of **12** and **13** followed by tosylation of the terminal hydroxy group and subsequent intramolecular alkylation of the nitrogen atom led to cephams **18** and **19**.



8 **9** **10** **11**

12: R= Tr
14: R= H
16: R= Ts

13: R= Tr
15: R= H
17: R= Ts

18 **19**

The absolute configuration of the azetidin-2-one fragment in **18** and **19** was determined by NOE measurements, thus proving the configuration of compounds **12-17**.

The present synthesis of the 1-oxacepham system offers excellent stereoselectivity and high yield at all steps. The stereochemical course of the cycloaddition to *cis* and *trans* olefins follows observations found by Effenberger[4] whereas the induction of absolute configuration takes the same direction as for compounds **1**. It should be stressed, as well, that *cis* configuration of 3-substituted-4-alkoxy-azetidine-2-one (compounds **12, 14, 16, 18**) would be difficult to obtain using methodology based on nucleophilic substitution of the acyloxy substituent at the C-4 carbon atom.

EXPERIMENTAL

Optical rotations were measured with a JASCO Dip-360 digital polarimeter. IR spectra were obtained with a FT-IR-1600 Perkin-Elmer spectrophotometer. ^{1}H NMR spectra were recorded using Varian Gemini 200 and Bruker AM 500 spectrometers. Mass spectra were obtained with an AMD 604 spectrometer. Column chromatography was performed on Merck Kiesel gel (230-400 mesh).

1,2-*O*-isopropylidene-5-*O*-trityl-α-D-xylofuranose (8) was obtained according to the known procedure.[7]

Z and E 3-*O*-(But-1-en-3-ynyl)-1,2-*O*-isopropylidene-5-*O*-trityl-α-D-xylofuranose (10 and 11). - A solution of 2,7-dihydroxy-2,7-dimethyl-octa-3,5-diyne (3.2 g, 20.0 mmol) in dry tetrahydrofuran (40 ml) was added dropwise to a stirred solution of compound **8** (4.3 g, 10.0 mmol) and pulverized potassium hydroxide (0.08 g) and tetrahydrofuran (25 ml) maintained under reflux. Stirring and heating were continued for 4 h until disappearance of the sugar substrate (tlc). Subsequently the mixture was cooled, filtered through Florisil, and concentrated. The syrup was dissolved in *t*-butyl methyl ether, washed, dried, evaporated and separated on a silica gel column using hexane: *t*-butyl methyl ether 9:1 $^v/_v$ as an eluent to afford **10** (1.3 g, 27%) and **11** (3.0 g, 63%). **10**: $[\alpha]_D$ -92.8° (*c* 0.65, CH_2Cl_2); IR (CCl_4): 1635, 2107, 3315 cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.32, 1.52 (2s, 6H, isopr.), 2.91 (dd, 1H, *J* 0.8 and 2.5 Hz, ≡CH), 3.36 (dd, 1H, *J* 8.1 and 9.2 Hz, H-5), 3.53 (dd, 1H, *J* 5.5 and 9.2 Hz, H-5'), 4.36 (m, 1H, H-4), 4.43 (d, 1H, *J* 3.0 Hz, H-3), 4.46 (dd, 1H, *J* 2.5 and 6.4 Hz CCH=), 4.61 (d, 1H, *J* 3.8 Hz, H-2), 5.93 (d, 1H, *J* 3.8 Hz, H-1), 6.38 (dd, 1H, *J* 0.8 and 6.4 Hz, OCH=), 7.1-7.5 (m, 15 H, trityl). Anal. Calcd for $C_{31}H_{30}O_5$: C, 77.18; H, 6.22. Found: C, 76.9; H, 6.4.
11: $[\alpha]_D$ -3.8° (*c* 2.0, CH_2Cl_2); IR (CCl_4): 1619, 1638, 2108, 3314 cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.30, 1.52 (2s, 6H, isopr.), 2.76 (d, 1H, *J* 2.4 Hz, ≡CH), 3.26, 3.46 (2m, 2H, H-5,5'), 4.35 (m, 2H, H-3,4), 4.52 (d, 1H, *J* 3.9 Hz, H-2), 4.94 (dd, 1H, *J* 2.4 and 12.8 Hz, CCH≡), 5.85 (d, 1H, *J* 3.9 Hz, H-1), 6.75 (d, 1H, *J* 12.8 Hz, OCH=), 7.1-7.5 (m, 15H, trityl). Anal. Calcd for $C_{31}H_{30}O_5$: C, 77.18; H, 6.22. Found: C, 77.0; H, 6.4.

Z 3-*O*-(But-1-enyl)-1,2-*O*-isopropylidene-5-*O*-trityl-α-D-xylofuranose (3). - Compound **10** (2.4 g, 5.0 mmol) in hexane-ethyl acetate 9:1 $^v/_v$ mixture (50 ml) was hydrogenated over palladium-barium sulfate (5%; 0.1 g) in the presence of quinoline (0.1 g) for 1 h. Subsequently the solution was passed through Florisil and evaporated. The residue was purified on a silica gel column using hexane *t*-butyl methyl ether as an eluent to give **3** (2.4 g, 99%). $[\alpha]_D$ -36.5° (*c* 0.65, CH_2Cl_2); IR (KBr) 1651, 1651 cm^{-1}; ^{1}H NMR ($CDCl_3$): 0.85 (t, 3H, CH_3), 1.32, 1.53 (2s, 6H, isopr.), 1.87 (m, 2H, CH_2), 3.34 (dd, 1H, *J* 7.2 and 9.2 Hz, H-5), 3.43 (dd, 1H, *J* 5.7 and 9.2 Hz, H-5'), 4.21 (d, 1H, *J* 3.0 Hz, H-3), 4.31-4.44 (m, 2H, H-4, CCH=), 4.53 (d, 1H, *J* 3.8 Hz, H-2), 5.88 (d, 1H, *J* 3.8 Hz, H-1), 5.92 (dt, 1H, *J* 1.5, 1.5 and 6.2 Hz, OCH=), 7.1-7.5 (m, 15 H, trityl). Anal. Calcd for $C_{31}H_{34}O_5$: C, 76.54; H, 6.99. Found: C, 75.8; H, 7.1.

E 3-*O*-(But-1-enyl)-1,2-*O*-isopropylidene-5-*O*-trityl-α-D-xylofuranose (4). -Compound **4** was obtained from **11** according to the procedure described above (97%). $[\alpha]_D$ -26.5° (*c* 0.29, CH_2Cl_2); IR (CCl_4): 1652, 1672 cm^{-1}; ^{1}H NMR ($CDCl_3$): 0.96 (t, 3H, CH_3), 1.32, 1.53 (2s, 6H, isopr.), 3.35 (dd, 1H, *J* 6.9 and 9.2 Hz, H-5), 3.40 (dd, 1H, *J* 5.6 and 9.2 Hz, H-5'), 4.27 (d, 1H, *J* 3.1 Hz, H-3), 4.36 (m, 1H, H-4), 4.55 (d, 1H, *J* 3.8 Hz, H-2), 4.92 (dt, 1H, *J* 7.0, 7.0 and 12.6 Hz, -CCH=), 5.86 (d, 1H, *J* 3.8 Hz, H-1), 6.09 (dt, 1H, *J* 1.3, 1.3 and 12.6 Hz, -OCH=), 7.1-7.5 (m, 15H, trityl). Anal. Calcd for $C_{31}H_{34}O_5$: C, 76.54; H, 6.99. Found: C, 76.2; H, 7.0.

(3'S, 4'R) 3-*O*-(3'-ethyl-azetidin-2'-on-4'-yl)-1,2-*O*-isopropylidene-5-*O*-trityl-α-D-xylofuranose (12). -To a suspension of anhydrous sodium carbonate (0.2 g) in anhydrous toluene (3 ml) chlorosulfonyl isocyanate (156 µl, 1.8 mmol) was added. The mixture was stirred and upon cooling to -78°C a solution of vinyl ether **3** (0.62 g, 1.2 mmol) in toluene (3 ml) was added dropwise. Stirring and cooling were maintained for 2.5 h. The suspension was cooled to -78°C, diluted with toluene (10 ml), treated with Red-Al (2.0 ml of a 1M solution in toluene), and left for 30 min whereas the temperature of reaction was maintained. Subsequently the temperature was allowed to rise to 0°C, water (1 ml) was added, and the solution was stirred for 30 min. The solution was filtered through Celite, evaporated and purified by chromatography using hexane: ethyl acetate

3:2 $^{v}/_{v}$ as an eluent to afford **12** (0.52 g, 80%). $[\alpha]_D$ -32.7° (*c* 0.36, CH_2Cl_2); IR (CH_2Cl_2): 1773, 3398 cm^{-1}; ^1H NMR ($CDCl_3$): 0.78 (t, 3H, CH_3), 1.33, 1.55 (2d, 6H, isopr.), 1.46 (m, 2H, CH_2), 2.84 (m, 1H, H-3'), 3.16 (dd, 1H, *J* 7.9 and 9.1 Hz, H-5a), 3.58 (dd, 1H, *J* 5.1 and 9.1 Hz, H-5b), 4.07 (d, 1H, *J* 3.1 Hz, H-3), 4.43 (ddd, 1H, *J* 3.1, 5.1 and 7.9 Hz, H-4), 4.54 (d, 1H, *J* 3.8 Hz, H-2), 5.01 (d, 1H, *J* 4.4 Hz, H-4'), 5.87 (d, 1H, *J* 3.8 Hz, H-1), 7.1-7.5 (m, 15H, trityl); MS (EI, HR) m/z: (M^++H) calcd for $C_{32}H_{35}NO_6$: 529.24643. Found: 529.246652.

(3'R, 4'R) 3-*O*-(3'-ethyl-azetidin-2'-on-4'-yl)-1,2-*O*-isopropylidene-5-*O*-trityl-α-D-xylofuranose (13). - Compound **13** was obtained from **4** according to the above procedure (75%). $[\alpha]_D$ -30.3° (*c* 0.67, CH_2Cl_2); IR (CH_2Cl_2): 1778, 3398 cm^{-1}; ^1H NMR ($CDCl_3$): 0.92 (t, 1H, CH_3), 1.32, 1.53 (2s, 6H, isopr.), 1.53, 1.64 (2m, 2H, CH_2), 2.91 (ddd, 1H, *J* 1.1, 6.6 and 8.2 Hz, H-3'), 3.18 (dd, 1H, *J* 8.9 and 9.2 Hz, H-5a), 3.55 (dd, 1H, *J* 5.3 and 9.2 Hz, H-5b), 4.06 (d, 1H, *J* 3.2 Hz, H-3), 4.35 (m, 1H, H-4), 4.51 (d, 1H, *J* 3.8 Hz, H-2), 4.79 (d, 1H, *J* 1.1 Hz, H-4'), 5.88 (d, 1H, *J* 3.8 Hz, H-1), 6.18 (bs, 1H, NH), 7.1-7.5 (m, 15H, trityl); MS (EI, HR) m/z: (M^++H) calcd for $C_{32}H_{35}NO_6$: 529.24643. Found: 529.246652.

(3'S, 4'R) 3-*O*-(3'-ethyl-azetidin-2'-on-4'-yl)-1,2-*O*-isopropylidene-α-D-xylofuranose (14). - Compound **11** was detritylated with 0.5% of p-TsOH in methanol at room temperature. The crude product was purified on a silica gel column using hexane: ethyl acetate 3:7 $^{v}/_{v}$ as an eluent to give **14** (75%). $[\alpha]_D$ +5.4° (*c* 0.5, CH_3OH); IR (film): 1759, 3300, 3413 cm^{-1}; ^1H NMR (acetone-d_6): 1.00 (t, 3H, CH_3), 1.27, 1.42 (2s, 6H, isopr.), 1.66 (m, 2H, CH_2), 3.13 (m, 1H, H-3'), 3.7-3.8 (m, 2H, H-5a, 5b), 4.11 (d, 1H, *J* 3.1 Hz, H-3), 4.23 (m, 1H, H-4), 4.68 (d, 1H, *J* 3.7 Hz, H-2), 5.28 (d, 1H, *J* 4.4 Hz, H-4'), 5.85 (d, 1H, *J* 3.7 Hz, H-1); MS (LSIMS, HR) m/z: (M^++H) calcd for $C_{13}H_{22}NO_6$: 288.14471. Found: 288.14471.

(3'R, 4'R) 3-*O*-(3'-ethyl-azetidin-2'-on-4'-yl)-1,2-*O*-isopropylidene-α-D-xylofuranose (15). - Compound **15** was obtained from **13** according to the above procedure (70%): $[\alpha]_D$ -12.3° (*c* 0.26, CH_3OH); IR (CH_2Cl_2): 1778, 3399, 3507 cm^{-1}; ^1H NMR ($CDCl_3$): 1.06 (t, 3H, CH_3), 1.33, 1.51 (2s, 6H, isopr.), 1.68, 1.80 (2m, 2H, CH_2), 3.05 (ddd, 1H, *J* 1.2, 6.3 and 8.6 Hz, H-3'), 3.80, 3.92 (2m, 2H, H-5a, 5b), 4.06 (d, 1H, *J* 3.4 Hz, H-3), 4.33 (dt, 1H, *J* 3.4 5.8 and 5.8 Hz, H-4), 4.57 (d, 1H, *J* 3.8 Hz, H-2), 5.96 (d, 1H, *J* 3.8 Hz, H-1), 6.31 (bs, 1H, NH); MS (LSIMS, HR) m/z: (M^++H) calcd for $C_{13}H_{22}NO_6$: 288.14471. Found: 288.14471.

(3'S, 4'R) 3-*O*-(3'-ethyl-azetidin-2'-on-4'-yl)-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-xylofuranose (16).- Compound **16** was obtained from **14** by a standard tosylation procedure (72%). $[\alpha]_D$ -20.0° (*c* 1.2, CH_2Cl_2): IR (film): 1766, 3330 cm^{-1}; ^1H NMR ($CDCl_3$): 0.98 (t, 3H, CH_3), 1.30, 1.46 (2s, 6H, isopr.), 1.57, 1.67 (2 m, 2H, CH_2), 2.46 (s, 3H, tosyl), 3.15 (tdd, 1H, H-3'), 4.04 (d, 1H, *J* 3.3 Hz, H-3), 4.12 (dd, 1H, *J* 5.4 and 9.8 Hz, H-5a), 4.22 (dd, 1H, *J* 7.5 and 9.8 Hz, H-5b), 4.40 (ddd, 1H, *J* 3.3, 5.4 and 7.5 Hz, H-4), 4.56 (d, 1H, *J* 3.7 Hz, H-2), 5.12 (d, 1H, *J* 4.4 Hz, H-4'), 5.87 (d, 1H, *J* 3.7 Hz, H-1), 6.39 (bs, 1H, NH), 7.37, 7.79 (2m, 4H, tosyl); MS (LSIMS, HR) m/z: (M^++H) calcd for $C_{20}H_{28}NO_8S$: 442.15356. Found: 442.15343.

(4'R, 4'R) 3-*O*-(3'-ethyl-azetidin-2'-on-4'-yl)-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-xylofuranose (17). - Compound **17** was obtained from **15** by a standard tosylation procedure (72%) $[\alpha]_D$ +2.5° (*c* 0.24, CH_3OH), IR (CH_2Cl_2): 1780, 3398 cm^{-1}; ^1H NMR ($CDCl_3$): 1.05 (t, 3H, CH_3), 1.30, 1.46 (2s, 6H, isopr.), 1.68, 1.79 (2m, 2H, CH_2), 2.46 (s, 3H, tosyl), 3.02 (ddd, 1H, *J* 1.2, 6.4 and 8.4 Hz, H-3'), 4.09 (d, 1H, *J* 3.2 Hz, H-3), 4.10 (dd, 1H, *J* 5.1 and 9.7 Hz, H-5a), 4.26 (dd, 1H, *J* 8.0 and 9.7 Hz, H-5b), 4.38 (ddd, 1H, *J* 3.2, 5.1 and 8.0Hz, H-4), 4.52 (d, 1H, *J* 3.7 Hz, H-2), 4.94 (d, 1H, *J* 1.2 Hz, H-4'), 5.08 (d, 1H, *J* 3.7 Hz, H-1), 6.34 (bs, 1H, NH), 7.37, 7.79 (2m, 4H, tosyl). MS (EI, HR) m/z: M^+ calcd for $C_{20}H_{27}NO_8S$: 441.14573. Found: 441.14553.

(3'S, 4'R) 5-Amino-5-deoxy-3-*O*:5-*N*-(3'-ethyl-azetidin-2'-on-4'-yl)-1,2-*O*-isopropylidene-α-D-xylofuranose (18). - Compound **18** was obtained from **16** according to the procedure described earlier; 90%; $[\alpha]_D$ +105.0° (*c* 0.4, CH_2Cl_2): IR (film): 1765 cm^{-1}; ^1H NMR ($CDCl_3$): 1.00 (t, 3H, CH_3). 1.33, 1.50 (2s, 6H, isopr.), 1.69 (quint, 2H, CH_2), 3.14 (m, 1H, H-3'), 3.50 (dt, 1H, *J* 1.5, 1.7 and 13.8 Hz, H-5a), 3.77 (dd, 1H, *J* 4.5 and 13.8 Hz, H-5b), 4.31 (d, 1H, *J* 3.2 Hz, H-3), 4.43 (ddd, 1H, *J* 1.5, 3.2 and 4.5 Hz, H-4), 4.63 (d, 1H, *J* 3.8 Hz, H-

2), 4.99 (d, 1H, *J* 3.5 Hz, H-4'), 5.97 (d, 1H, *J* 3.8 Hz, H-1); MS (LSIMS, HR) m/z: M(⁺+H) calcd for $C_{13}H_{20}NO_5$: 270.13414. Found: 270.14313.

(3'R,4'R) 5-Amino-5-deoxy-3-*O*:5-*N*-(3'-ethyl-azetidin-2'-on-4'-yl)-1,2-*O*-isopropylidene-α-D-xylofuranose (**19**).- Compound **19** was obtained from **17** according to the procedure described earlier; 93%; $[\alpha]_D$ +114.4° (*c* 0.64, CH_2Cl_2): IR (film): 1763 cm^{-1}; ^1H NMR ($CDCl_3$): 1.02 (t, 3H, CH_3), 1.33, 1.49 (2s, 6H, isopr.), 1.67, 1.77 (2m, 2H, CH_2), 2.91 (dd, 1H, *J* 6.3 and 8.2 Hz, H-3'), 3.53 (dd, 1H, *J* 1.8 and 13.8 Hz, H-5a), 3.79 (dd, 1H, *J* 4.5 and 13.8 Hz, H-5b), 4.31 (dd, 1H, *J* 0.4 and 3.2 Hz, H-3), 4.42 (ddd, 1H, *J* 1.8, 3.2 and 4.5 Hz, H-4), 4.62 (d, 1H, *J* 3.8 Hz, H-2), 4.71 (d, 1H, *J* 0.4 Hz, H-4'), 5.97 (d, 1H, *J* 3.8 Hz, H-1): MS (EI, HR) m/z: M^+ calcd for $C_{13}H_{19}NO_5$: 269.12632. Found: 269.12634.

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