Pergamon

Tetrahedron: *Asymmetry* 11 (2000) 2015–2022

TETRAHEDRON: *ASYMMETRY*

Diastereoselection in 1,3-dipolar cycloadditions of a chiral cyclic nitrone to α,β-unsaturated δ-lactones

M. Jurczak,[a] J. Rabiczko,[a] D. Socha,[a] M. Chmielewski,[a,*] F. Cardona,[b] A. Goti[b] and A. Brandi[b,*]

[a]*Institute of Organic Chemistry of the Polish Academy of Sciences, 01-224 Warsaw, Poland*
[b]*Dipartamento di Chimica Organica 'U. Schiff', Centro dei Composti Eterociclici-CNR, Universita di Firenze, I-50121 Firenze, Italy*

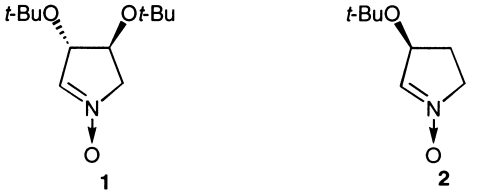
Received 21 March 2000; accepted 29 March 2000

Abstract

1,3-Dipolar cycloadditions of the nitrone **1** to α,β-unsaturated δ-lactones: non-chiral **13**, racemic mixture **3**/**4**, D-*glycero* **3**, and L-*glycero* **4** proceed with high stereoselectivity in the cases of **13** and **3** and a significant kinetic resolution in the case of the racemate **3**/**4**. The *exo* approach to the *re–re* sides of the lactones predominates. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Bicyclic isoxazolidines, readily available via 1,3-dipolar cycloaddition of the five-membered cyclic nitrones **1** and **2**, derived from tartaric acid[1] and malic acid,[2] to olefins open an entry to a variety of iminosugars which display biological activity as glycosidase inhibitors[3] (Scheme 1). The usefulness of the isoxazolidine approach to iminosugars has been demonstrated in a large number of examples,[2,4] since the nitrones **1** and **2** usually offer good regio- and stereoselectivities with the introduction of convenient functionalities.

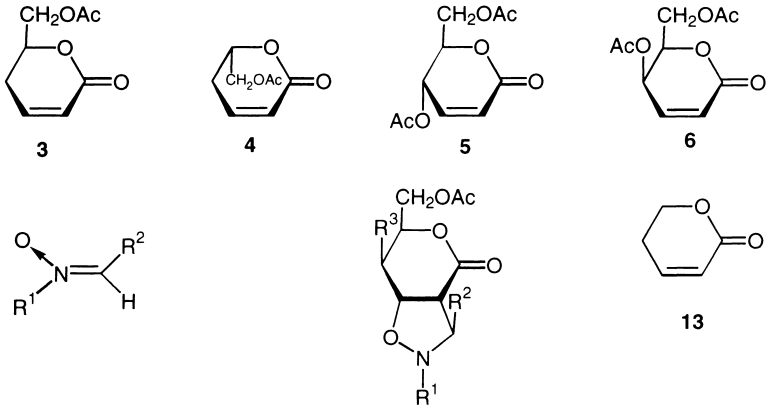


Scheme 1.

* Corresponding authors. E-mail: chmiel@icho.edu.pl

PII: S0957-4166(00)00126-9

The readily available racemic lactone **3**/**4**,[5] its D-*glycero* enantiomer **3**,[6] D-*erythro* compound **5** and D-*threo* **6**[7] have been investigated by some of us in conjugate additions with hydroxylamines[8] and hydrazines,[9] as well as in 1,3-dipolar cycloaddition to nitrones[10] (Scheme 2). It has been found that 1,3-dipolar cycloaddition of nitrones **7**–**11** to lactones **3** and **6** proceeds with high regio- and stereoselectivity to afford the *anti–endo* adducts **12**. The previously[11] found low stereoselectivity in the case of diaromatic nitrone **11** was a consequence of not only its *exo*:*endo* approach to lactones **5** and **6**, but also of the fact that the temperature of the reaction (boiling toluene) caused an equilibration of the *Z* and *E* isomers of the 1,3-dipole.[12]



7: R^1 = Bn; R^2 = H
8: R^1 = Bn; R^2 = CH_3
9: R^1 = PMB; R^2 = H
10: R^1 = PMB; R^2 = CH_3
11: R^1 = Ph; R^2 = p-$CH_3OC_6H_4$

12: R^1 = Bn, PMB;
R^2 = H, CH_3
R^3 = H, OAc

Scheme 2.

2. Results and discussion

In this paper we report 1,3-dipolar cycloaddition reactions of **1** with non-chiral lactone **13**, racemic mixture **3**/**4**, D-*glycero* **3** and L-*glycero* lactone **4**. The reactions were carried out in toluene at room temperature, or under reflux, to afford non-separable mixtures of diastereomers. The ratios of respective products are presented in Table 1.

The lactone **13** reacted with **1** to give the almost pure adduct **14** in 91% yield as the result of the *exo* approach of the dipole to the *re–re* side of the dipolarophile (Fig. 1). Signals arising from the alternative diastereomer **15** were found in the NMR spectrum of the crude **14**. The configuration of adduct **14** was proven by NOE experiments (Fig. 2) which showed the enhancement of the intensity of the signal H-6 (δ 4.13) by 10.1% when H-5a (δ 3.58) was irradiated. Conversely, the signal due to H-5a was enhanced by 11.1% when H-6 was irradiated. NOE experiments did not show any spin–spin interaction between H-5a and H-5b (δ 3.73). In addition, irradiation of

Table 1
1,3-Dipolar cycloaddition of nitrone **1** to lactones **13**, **3**, **3**/**4** and **4**

Entry	Lactone	Lactone:**1** Ratio	Yield %	Proportion of stereoisomers (%)		Reaction conditions
1	**13**	1:1 (0.5mmol : 0.5mmol)	91	**14** (97)	**15** (3)	r.t., 48h
2	**3**	1:1 (0.5mmol : 0.5mmol)	88	**16** (100)		r.t., 48h
3	**3/4**	1:1 (0.5mmol : 0.5mmol)	78	**16** (65)	**17** (35)	r.t., 24h and reflux, 30min
4	**3/4**	2:1 (0.8mmol : 0.4mmol)	86	**16** (91)	**17** (9)	r.t., 48h
5	**4***	1:1 (0.35mmol : 0.35mmol)	74	**16** (15)	**17** (85)	r.t., 24h and reflux, 30min

*optical purity 77.4% e.e.

H-1a (δ 4.70) enhanced the intensity of H-8′ absorption (δ 2.78) by 5.7%, whereas H-8′ did not show any spin–spin interaction with H-7 (δ 3.70). We were not able to prove the geometry of the side product **15**. The structure and configuration of **15** was assigned on the assumption of the alternative, unfavoured, *exo* approach of **1** to the *si–si* side of the lactone **13** (Fig. 1).

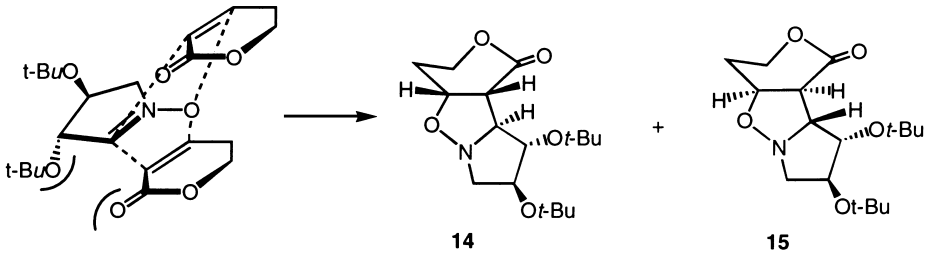


Figure 1. Stereochemical model of 1,3-dipolar cycloaddition of nitrone **1** to lactone **13**

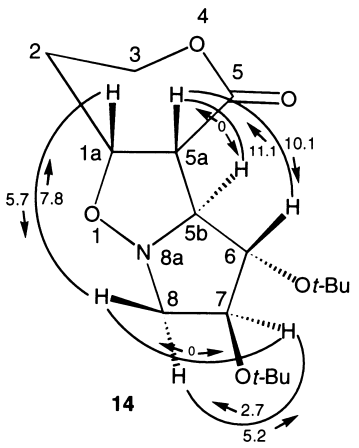


Figure 2. Observed NOEs demonstrating the *exo* approach of **1** to the *re–re* side of lactone **13**

The lactone **3** reacts with **1** to give a single product **16** (Fig. 3). The NMR spectra of **16** in $CDCl_3$ and in C_6D_6 were not well resolved and consequently we could not use NOEs to assign the configuration. The NMR spectrum of **16**, however, shows striking similarities to the spectrum of **14**, in chemical shifts and coupling constants (cf. Experimental). Therefore we ascribed the same configuration of the isoxazolidine ring protons to both compounds. Hydrogenolysis of the N–O in **16** followed by *N*-acetylation afforded compound **18**. The coupling constants pattern of the lactone part indicated the $^4C_1$ conformation, thus proving the configuration of the adduct **16**.

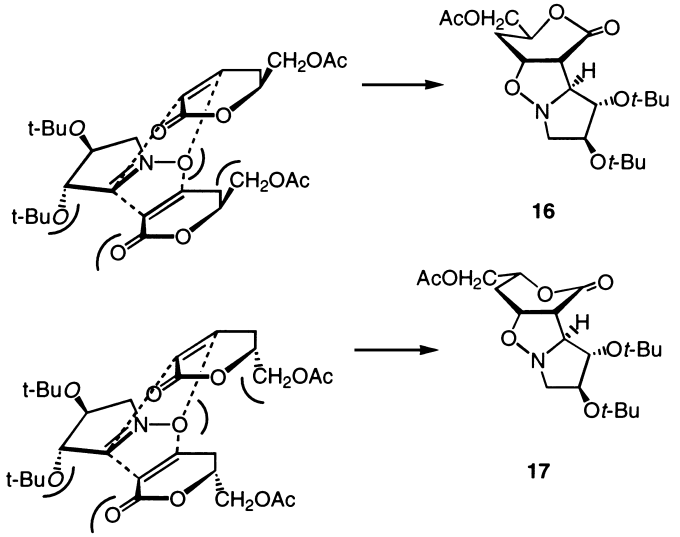
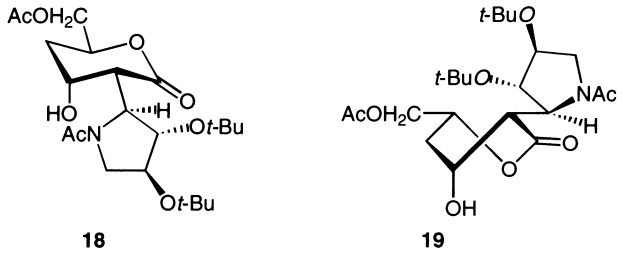


Figure 3. Schematic pathway of 1,3-dipolar cycloaddition of nitrone **1** to lactones **3** and **4**

The racemic lactone **3**/**4** treated with **1** gave an inseparable mixture of the two diastereomers **16** and **17** in a proportion of 65:35, respectively (Fig. 3). In the case of two molar excess of the racemate **3**/**4** being used, the ratio of **16**:**17** changed to 91:9, respectively, showing a significant kinetic resolution of the substrate. The unreacted lactone **4** was recovered and showed an optical activity corresponding to 77% e.e. The enriched lactone **4**, when subjected to cycloaddition with **1** afforded a mixture of **16** and **17** in a ratio of 15:85, respectively, reflecting the e.e. of **4** and confirming the high diastereoselectivity of the process.

Hydrogenolysis of the N–O bond in **17** (70% d.e.) gave the lactone **19**. A comparison of NMR spectra of **18** and **19** is consistent with a twist-$^2T_3$ conformation for **19**, thus proving the configuration of the adduct **17**.

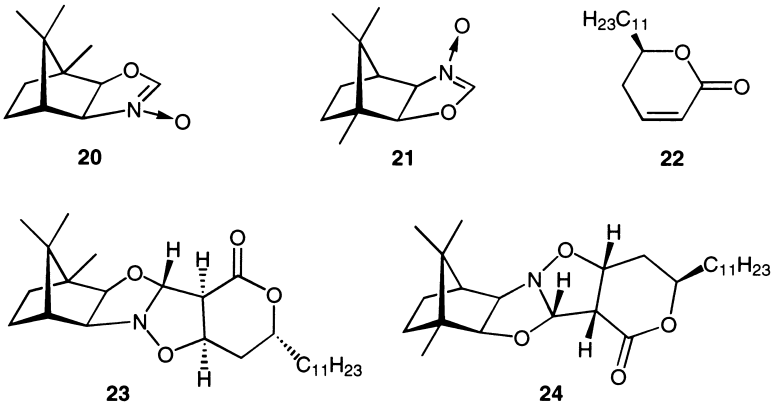
The previous results of 1,3-dipolar cycloaddition of **1** to cyclic α,β-unsaturated phosphine oxides,[13] as well as examination of Dreiding models of nitrone **1** and dipolarophiles **13**, **3** and **4**, indicate that only an *exo* approach of the reactants is possible. Moreover, the steric hindrance of the 3-*t*-butoxy substituent in nitrone **1** helps to ascertain the approach to the *si–si* side of the lactone as unfavourable (Fig. 2). This is easily seen if one compares the additions of **1** to **13** and **3**. In the case of **4**, the *exo* approach to the *re–re* side of the dipolarophile proceeds *syn* to the terminal acetoxymethyl group of the lactone. Consequently, it is less favoured and leads to the kinetic resolution of the racemate **3**/**4** (Scheme 3).



18 19

Scheme 3.

A similar cycloaddition of chiral oxazoline *N*-oxides **20** and **21** to the analogous α,β-unsaturated δ-lactone **22** has recently been reported by Langlois et al.[14] (Scheme 4). Despite the different nature of the nitrones, these authors also found the same stereochemical preferences. The cycloaddition between **20** and **21** proceeded smoothly to form a matched pair affording the *anti–exo* product **23**, whereas **21** and **22** formed a mismatched pair leading to the *anti–endo* product **24** in a low yield only.



20 21 22 23 24

Scheme 4.

In summary, we have demonstrated high stereoselectivity in 1,3-dipolar cycloaddition of the nitrone **1** to the sugar derived lactones **13** and **3**, and an effective kinetic resolution of the racemic lactone **3**/**4**. The highest d.e. of **16** (82%) and the highest purity of unreacted **4** (e.e. 77%) were observed when two equivalents of the dipolarophile were used. It is worthy to note that nitrones **1** and **2** gave moderate to very good kinetic resolutions[13,15] with other dipolarophiles.

3. Experimental

^{1}H NMR spectra were recorded for solutions on a Bruker DRX 500 Avance spectrometer. IR spectra were obtained on an FT-IR-1600 Perkin–Elmer spectrophotometer. Rotations were measured with a JASCO Dip-360 digital polarimeter. Column chromatography was performed on Merck silica gel 230–400 mesh.

Racemic lactone **3**/**4** was obtained according to Ref. 5. D-*glycero* Lactone **3** was obtained from **5** using Roth and Roark procedure;[6] $[\alpha]_D$ –105.5 (*c* 1.0, CH_2Cl_2).

3.1. Cycloaddition of nitrone **1** to lactones **13**, **3**, **3**/**4**, **4**. General procedure

The lactone and nitrone **1** in the ratios reported in Table 1 were dissolved in dry toluene (3 ml) and stirred at room temperature for 48 h (entries 1, 2 and 4) or for 24 h and then under reflux for 30 min (entries 3 and 5). The progress of the reaction was monitored by TLC. After removal of the solvent, the residue was purified on a silica gel column to afford corresponding cycloadducts as non-separable mixtures.

3.1.1. (*1a*R,*5a*R,*5b*S,*6*S,*7*S)-6,7-Di-tert-butoxy-5-oxo-pyrrolidino[1,2-b]isoxazolidino[4,5-c]tetrahydropyran **14**

Diastereomeric excess: 94%; $[\alpha]_D$ +42.5 (*c* 1.0, CH_2Cl_2); IR (film): 2975, 1733 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 4.70 (m, 1H, H-1a), 4.49 (ddd, 1H, *J* 11.3, 10.3, 2.6 Hz, H-3), 4.23 (dddd, 1H, *J* 11.3, 4.8, 3.8, 1.1 Hz, H-3′), 4.13 (bs, 1H, H-6), 3.90 (ddd, 1H, *J* 5.8, 4.2, 2.0 Hz, H-7), 3.73 (bd, 1H, *J* 6.4 Hz, H-5b), 3.70 (dd, 1H, *J* 12.5, 6.0 Hz, H-8), 3.58 (dd, 1H, *J* 8.3, 6.4 Hz, H-5a), 2.78 (dd, 1H, *J* 12.5, 4.2 Hz, H-8′), 2.14 (m, 1H, *J* 15.0, 10.8, 4.4, 3.8 Hz, H-2), 1.93 (m, 1H, *J* 15.0, 4.8, 4.0, 2.7 Hz, H-2′), 1.21 and 1.17 (2s, 18H, 2O*t*-Bu). Anal. calcd for $C_{17}H_{29}NO_5$ (327.42): C, 62.36; H, 8.93; N, 4.28. Found: C, 62.3; H, 8.8; N, 4.1.

3.1.2. (*1a*S,*5a*S,*5b*R,*6*S,*7*S)-6,7-Di-tert-butoxy-5-oxo-pyrrolidino[1,2-b]isoxazolidino[4,5-c]tetrahydropyran **15**

^1H NMR (500 MHz, $CDCl_3$) δ signals visible in the spectrum of **14** (~3%): 4.05 (dd, 1H, *J* 7.1, 6.0 Hz, H-6), 3.95 (ddd, 1H, *J* 7.6, 6.7, 6.0 Hz, H-7), 3.65 (dd, 1H, *J* 7.4, 2.5 Hz, H-5a), 3.26 (dd, 1H, *J* 13.4, 6.7 Hz, H-8), 3.00 (dd, 1H, *J* 13.4, 7.6 Hz, H-8′).

3.1.3. (*1a*R,*3*S,*5a*R,*5b*S,*6*S,*7*S)-3-Acetoxymethyl-6,7-di-tert-butoxy-5-oxo-pyrrolidino[1,2-b]isoxazolidino[4,5-c]tetrahydropyran **16**

$[\alpha]_D$ +46.7 (*c* 1.0, CH_2Cl_2); IR (film): 2975, 1743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 4.79 (m, 1H, *J* 11.1, 5.3, 3.6, 2.8 Hz, H-3), 4.71 (ddd, 1H, *J* 7.6, 3.3, 2.4 Hz, H-1a), 4.25 (dd, 1H, *J* 12.2, 3.6 Hz, C$\mathbf{H_A}H_B$OAc), 4.20 (dd, 1H, *J* 12.2, 5.3 Hz, $CH_A\mathbf{H_B}$OAc), 4.15 (bs, 1H, H-6), 3.90 (m, 1H, *J* 5.9, 4.0, 2.0 Hz, H-7), 3.71 (dd, 1H, *J* 12.6, 5.9 Hz, H-8), 3.66 (bd, 1H, *J* 6.4 Hz, H-5b), 3.63 (dd, 1H, *J* 7.6, 6.4 Hz, H-5a), 2.78 (dd, 1H, *J* 12.6, 4.0 Hz, H-8′), 2.09 (s, 3H, OAc), 2.01 (ddd, 1H, *J* 15.1, 2.8, 2.4 Hz, H-2), 1.95 (ddd, 1H, *J* 15.1, 11.1, 3.8 Hz, H-2′), 1.21 and 1.17 (2s, 18H, 2O*t*-Bu). Anal. calcd for $C_{20}H_{33}NO_7$ (399.48): C, 60.13; H, 8.33; N, 3.51. Found: C, 60.3; H, 8.4; N, 3.4.

3.1.4. (*1a*R,*3*R,*5a*R,*5b*S,*6*S,*7*S)-3-Acetoxymethyl-6,7-di-tert-butoxy-5-oxo-pyrrolidino[1,2-b]isoxazolidino[4,5-c]tetrahydropyran **17**

Diastereomeric excess: 70%; $[\alpha]_D$ +7.9 (*c* 1.0, CH_2Cl_2); IR (film): 2975, 1744 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 4.92 (m, 1H, *J* 11.6, 5.2, 3.4, 2.5 Hz, H-3), 4.45 (m, 1H, *J* 6.7, 3.0, 2.9 Hz, H-1a), 4.27 (dd, 1H, *J* 12.2, 3.4 Hz, C$\mathbf{H_A}H_B$OAc), 4.18 (dd, 1H, *J* 12.2, 5.2 Hz, $CH_A\mathbf{H_B}$OAc), 4.07 (dd, 1H, *J* 6.9, 2.1 Hz, H-5b), 4.06–3.98 (m, 2H, H-6,7), 3.69 (dd, 1H, *J* 6.7, 2.1 Hz, H-5a), 3.29 (dd, 1H, *J* 13.2, 6.2 Hz, H-8), 2.97 (dd, 1H, *J* 13.2, 7.1 Hz, H-8′), 2.09 (s, 3H, OAc), 2.04 (ddd, 1H, *J* 14.8, 2.9, 2.5 Hz, H-2), 1.94 (ddd, 1H, *J* 14.8, 11.6, 3.0 Hz, H-2′), 1.25 and 1.17 (2s, 18H, 2O*t*-Bu). Anal. calcd for $C_{20}H_{33}NO_7$ (399.48): C, 60.13; H, 8.33; N, 3.51. Found: C, 60.0; H, 8.5; N, 3.4.

3.2. Hydrogenolysis of cycloadducts **16** and **17** (70% d.e.). General procedure

Cycloadduct **16** or **17** (60 mg, 0.15 mmol) was dissolved in methanol (4 ml) and hydrogenated over 5% Pd/C (25 mg) at room temperature under atmospheric pressure for 2 h. Subsequently, the catalyst was filtered off and methanol was evaporated. The crude residue was acetylated with acetic anhydride–pyridine mixture in the presence of DMAP. The solvent was evaporated and the product was purified on a silica gel column to afford diastereomerically pure compound **18** or **19**, respectively.

3.2.1. (2′S,3′S,4′S)-N-*Acetyl-6*-O-*acetyl-3′,4′-di*-tert-*butoxy-2,4-dideoxy-2*-C-*pyrrolidin-2′-yl-D*-ribo-*aldono-1,5-lactone* **18**

Yield 69%; $[\alpha]_D$ +25.3 (*c* 0.7, CH_2Cl_2); IR (film): 3304, 2975, 1742, 1625 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$+D_2O) δ: 4.97 (m, 1H, *J* 12.0, 5.2, 4.2, 3.2 Hz, H-5), 4.53 (bs, 1H, H-3′), 4.32 (bd, 1H, *J* 10.7 Hz, H-2), 4.26 (dd, 1H, *J* 12.1, 3.2 Hz, H-6), 4.17 (dd, 1H, *J* 12.1, 5.2 Hz, H-6a), 4.06 (m, 1H, *J* 4.4, 1.9, 1.8 Hz, H-3), 3.93 (bd, 1H, *J* 5.2 Hz, H-4′), 3.84 (ddd, 1H, *J* 10.8, 5.2 Hz, H-5′), 3.27 (dd, 1H, *J* 10.7, 1.8 Hz, H-2), 3.23 (d, 1H, *J* 10.8 Hz, H-5′a), 2.14 and 2.06 (2s, 6H, 2Ac), 2.10 (m, 1H, *J* 13.8, 4.4, 4.2 Hz, H-4), 1.73 (m, 1H, *J* 13.8, 12.0, 1.9 Hz, H-4a), 1.26 and 1.16 (2s, 18H, 2O*t*-Bu). Anal. calcd for $C_{22}H_{37}NO_8$ (443.54): C, 59.58; H, 8.41; N, 3.16. Found: C, 59.4; H, 8.6; N, 3.1.

3.2.2. (2′S,3′S,4′S)-N-*Acetyl-6*-O-*acetyl-3′,4′-di*-tert-*butoxy-2,4-dideoxy-2*-C-*pyrrolidin-2′-yl-L*-lyxo-*aldono-1,5-lactone* **19**

Yield 61%; $[\alpha]_D$ –27.4 (*c* 0.85, CH_2Cl_2); IR (film): 3321, 2974, 1743, 1626 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$+D_2O) δ: 4.98 (m, 1H, H-5), 4.57 (dd, 1H, *J* 9.2, 6.0 Hz, H-2′), 4.29 (dd, 1H, *J* 12.1, 3.3 Hz, H-6), 4.28 (m, 1H, H-3′), 4.17 (dd, 1H, *J* 12.1, 5.1 Hz, H-6a), 4.09 (m, 1H, H-3), 3.89 (m, 1H, H-4′), 3.55 (dd, 1H, *J* 10.9, 3.5 Hz, H-5′), 3.35 (dd, 1H, *J* 10.9, 1.2 Hz, H-5′a), 2.99 (d, 1H, *J* 9.2 Hz, H-2), 2.15–2.06 (m, 1H, H-4), 2.12 and 2.04 (2s, 6H, 2Ac), 1.89 (m, 1H, *J* 13.7, 11.7, 2.0 Hz, H-4a), 1.20 and 1.19 (2s, 18H, 2O*t*-Bu). Anal. calcd for $C_{22}H_{37}NO_8$ (443.54): C, 59.58; H, 8.41; N, 3.16. Found: C, 59.7; H, 8.5; N, 3.2.

Acknowledgements

Authors thank PAN (Polish Academy of Sciences, Warsaw) and CNR (National Research Council, Rome) for the bilateral cooperation, and the State Committee for Scientific Research and the Ministry of University and Scientific and Technological Research (MURST Cofin 1998–2000, Italy) for financial support.

References

1. (a) Cicchi, S.; Höld, I.; Brandi, A. *J. Org. Chem.* **1993**, *58*, 5274; (b) Ballini, R.; Marcantoni, E.; Petrini, M. *J. Org. Chem.* **1992**, *57*, 1316.
2. Cicchi, S.; Goti, A.; Brandi, A. *J. Org. Chem.* **1995**, *60*, 4743.
3. (a) Elbein, A. D.; Molyneux, R. J. In *The Alkaloids*: *Chemical and Biological Perspectives*; Pelletier, S. W., Ed.; Wiley-Interscience: New York, 1987; Vol. 5, Chapter 1; (b) Howard, A. S.; Michael, J. P. In *The Alkaloids*; Brossi, A., Ed.; Academic Press: New York, 1986; Vol. 28, Chapter 3; (c) Elbein, A. D. *Ann. Rev. Biochem.* **1987**, *56*, 597;

(d) Winchester, B.; Fleet, G. W. J. *Glycobiology* **1992**, *2*, 199; (e) Legler, G. *Adv. Carbohydr. Chem. Biochem.* **1990**, *48*, 319. (f) Fellows, L. E. *Chem. Ber.* **1987**, *23*, 842; (g) Sinnott, M. L. *Chem. Rev.* **1990**, *90*, 1171; (h) Wong, C.-H.; Halcomb, R. L.; Ichibaka, Y.; Kajimoto, T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 521; (i) Frank, R. W. *Bioorg. Chem.* **1992**, *20*, 77.

4. (a) Brandi, A.; Cicchi, S.; Cordero, F. M.; Frignoli, R.; Goti, A.; Picasso, S.; Vogel, P. *J. Org. Chem.* **1995**, *60*, 6806; (b) Cardona, F.; Valenza, S.; Goti, A.; Brandi, A. *Tetrahedron Lett.* **1997**, *38*, 8097; (c) Cardona, F.; Valenza, S.; Picasso, S.; Goti, A.; Brandi, A. *J. Org. Chem.* **1998**, *63*, 7311; (d) Cardona, F.; Salanski, P.; Chmielewski, M.; Valenza, S.; Goti, A.; Brandi, A. *Synlett* **1998**, 1444.
5. Mieczkowski, J.; Jurczak, J.; Chmielewski, M.; Zamojski, A. *Carbohydr. Res.* **1977**, *56*, 180.
6. Roth, B. D.; Roark, W. H. *Tetrahedron Lett.* **1988**, *29*, 1255.
7. (a) Chmielewski, M.; Jurczak, J.; Maciejewski, S. *Carbohydr. Res.* **1987**, *165*, 111; (b) Lichtenthaler, F. W.; Röninger, S.; Jarglis, P. *Liebigs Ann. Chem.* **1989**, 1153.
8. (a) Panfil, I.; Maciejewski, S.; Belzecki, C.; Chmielewski, M. *Tetrahedron Lett.* **1989**, *30*, 1527; (b) Maciejewski, S.; Panfil, I.; Belzecki, C.; Chmielewski, M. *Tetrahedron* **1992**, *48*, 10363.
9. (a) Panfil, I.; Chmielewski, M. *Heterocycles* **1993**, *36*, 2267; (b) Panfil, I.; Krajewski, J.; Gluzinski, P.; Stefaniak, L.; Chmielewski, M. *Tetrahedron* **1994**, *50*, 7219.
10. Panfil, I.; Belżecki, C.; Urbanczyk-Lipkowska, Z.; Chmielewski, M. *Tetrahedron* **1991**, *47*, 10087.
11. Panfil, I.; Chmielewski, M. *Tetrahedron* **1985**, *47*, 4713.
12. (a) Torssell, K. B. G. *Nitrile Oxides, Nitrones and Nitronates in Organic Synthesis*; VCH Publishers Inc.: New York, 1988; (b) Frag, M. J.; Thomas, E. J.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2763.
13. Brandi, A.; Cicchi, S.; Goti, A.; Koprowski, M.; Pietrusiewicz, K. M. *J. Org. Chem.* **1994**, *59*, 1315.
14. Dirat, O.; Konklovsky, C.; Langlois, Y.; Lesot, Ph.; Courtieu, J. *Tetrahedron: Asymmetry* **1999**, *10*, 3197.
15. (a) Cardona, F.; Valenza, S.; Goti, A.; Brandi, A. *Eur. J. Org. Chem.* **1999**, 1319. (b) Pietrusiewicz, K. M.; Holody, W.; Koprowski, M.; Cicchi, S.; Goti, A.; Brandi, A. *Phosphorus, Sulfur and Silicon* **1999**, *146*, 389.