Pergamon

Tetrahedron: *Asymmetry* 9 (1998) 1269–1276

TETRAHEDRON: *ASYMMETRY*

Straightforward synthesis of a derivative of purpurosamine C from D-galactose

Patricia A. Zunszain and Oscar Varela *

CIHIDECAR (CONICET) — Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón 2, 1428 Buenos Aires, Argentina

Received 13 January 1998; accepted 15 February 1998

Abstract

Purpurosamine C (**1**) is a component of the aminoglycoside antibiotic gentamicin C_{1a}. A derivative of **1** was synthesized from D-galactose via its 2-acetoxy-3,4,6-tri-*O*-acetyl glycal (**3**). Compound **3** undergoes glycosylation with 2-propanol in the presence of $SnCl_4$, with two succesive allylic rearrangements of the double bond to give isopropyl 6-*O*-acetyl-3,4-dideoxy-α-D-*glycero*-hex-3-enopyranosid-2-ulose (**7**). Compound **7** was hydrogenated, and *O*-deacetylated to afford **8**. The free OH group of **8** was tosylated and substituted by azide, and the carbonyl function of the resulting ulose **10** reacted with hydroxylamine to give the *E,Z*-oximes (**11,12**). Highly diastereoselective reduction of the oxime acetate (**13**) by borane, which also reduced the azide function, led to the purpurosamine C derivative **14** (~40% yield from **3**).

1. Introduction

Purpurosamine C (**1**) is one of the components of the broad spectrum antibiotic gentamicin C_{1a}, produced by *Micromonospora purpurea*.[1] It is also a constituent of semisynthetic aminoglycoside antibiotics of the 3′,4′-dideoxykanamycin type, such as dibekacin and arbekacin.[2,3] Several syntheses of derivatives of this diaminotetradeoxyhexose have been reported. The sigmatropic rearrangement of an allylic thiocyanate[4] (which isomerizes to isothiocyanate) or azide[5–7] was the key step in some syntheses. Levoglucosenone[8] and glucosamine[9,10] have been employed as starting materials for the synthesis of derivatives of purpurosamine C. Also, non-carbohydrate precursors have been used to prepare purpurosamine C in racemic form. Thus, addition of nitrosyl chloride to 2-acetoxymethyl-3,4-dihydro-2*H*-pyran,[11] or [4+2] cycloaddition of a diene to a 2-amino aldehyde[12] led to the diaminosugar. Alternatively, addition of *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam to a diene,[13] or cycloaddition from a carbohydrate precursor,[14] led to enantiomerically pure purpurosamine C derivatives.

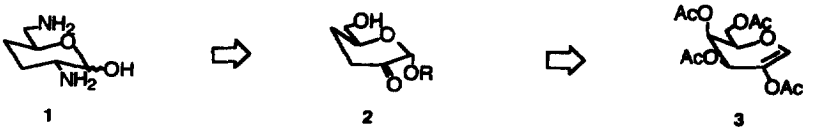
* Corresponding author. E-mail: varela@qo.fcen.uba.ar

0957-4166/98/$19.00
PII: S0957-4166(98)00083-4

The above-mentioned syntheses are commonly multi-step procedures and the overall yields are relatively low. We wish to report here a straightforward route to purpurosamine C, starting from inexpensive and commercially available galactose, via its 2-acetoxy glycal triacetate (**3**).

2. Results and discussion

The retrosynthetic analysis of purpurosamine C (Scheme 1) suggests a dideoxyulose derivative (**2**) as a convenient synthon, since the 6-OH group can be readily converted into an amine and the carbonyl at C-2 is a good precursor of the other amino group. The synthesis of such an ulose from a monosaccharide would require a rather complex sequence of selective protections of hydroxyl groups, oxidation, elimination and reduction. However, we have found in our laboratory[15] that Lewis acid catalyzed glycosylation of 2-acyloxyglycals leads to enulose derivatives in a single step. Thus, 2-acetoxy-3,4,6-tri-*O*-acetyl-D-galactal (**3**), readily obtained from D-galactose,[16] underwent the tin(IV) chloride promoted glycosylation to give the enulose **4**, in 90% yield. Compound **4** arises from the addition of 2-propanol to the anomeric center with Ferrier's rearrangement of the double bond.[17] The vinylic acetate of the resulting enopyranoside is attacked by the alcohol promoting a second allylic rearrangement, with elimination of the acetoxy substituent at C-4 and generation of the enone system. The remarkable diastereoselectivity in the formation of the glycosylic linkage may be attributed to the anchimeric participation of the acetoxy group at C-2. This group can stabilize the positive charge at C-1 by formation of an acyloxonium ion having a β-configuration, because of the stereoelectronic requirement of a positively charged anomeric substituent[18] (reverse anomeric effect). Therefore, the attack of the alcohol should take place from the opposite face, leading to the α-glycosylic bond.

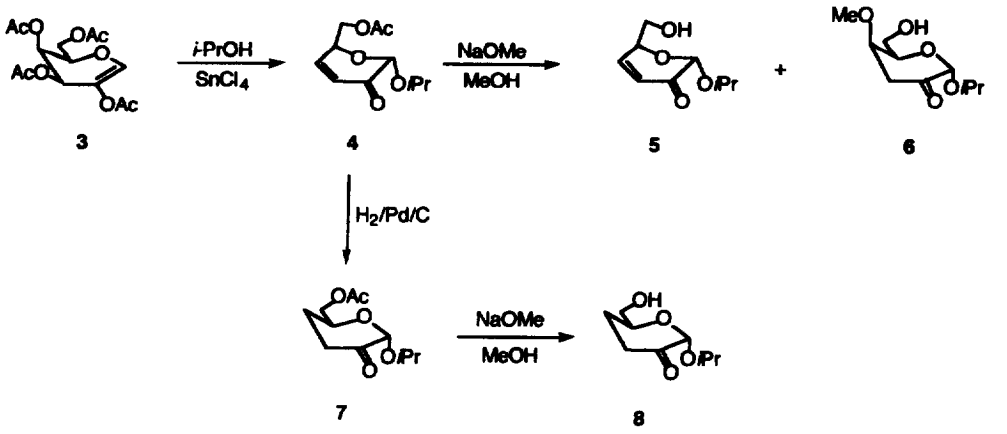


1 2 3

Scheme 1.

Attempted deacetylation of **4** afforded the desired derivative **5**, having the free hydroxyl group at C-6, together with a considerable amount of the Michael addition product **6** (Scheme 2). The configuration of the stereocenter at C-4 of the major isomer was determined to be *R* by means of its ^{1}H NMR spectrum (Table 1). Thus, the small $J_{3,4}$ and $J_{3',4}$ (3.4 and 3.1 Hz, respectively) indicated that H-4 bisects the H–C(3)–H′ angle, and hence that the methoxy substituent is quasiaxially oriented. This result is also confirmed by the small value of $J_{4,5}$ (~1 Hz). In order to avoid the formation of **6**, compound **4** was hydrogenated to give **7**, which was treated with sodium methoxide to afford **8** (93% yield from **4**). The ^{13}C NMR spectrum of **8** (Table 2) showed the resonances of the anomeric and the carbonyl carbons at 202.9 and 97.8 ppm, respectively. The signals of the carbons bonded to oxygen (C-5 and C-6) appeared at 68.8 and 64.8 ppm, and those of the methylene carbons at 34.7 and 28.7 ppm. Compound **8** is identical to **2**, the direct precursor of purpurosamine proposed in the retrosynthetic analysis (Scheme 1). Tosylation of crude **8** gave **9** in 94% overall yield from **7** (Scheme 3).

Nucleophilic displacement of the tosylate group of **9** by sodium azide in DMF at 80°C (18 h) led to the azide derivative **10** in 82% yield. The substitution of tosylate by azide produces in the ^{13}C NMR spectra a strong shift for the C-6 signal from 71.0 to 54.2 ppm. The ^{1}H NMR spectra of **9** and **10** also showed significant changes. For example, the double doublets of the methylene protons vicinal to the tosylate (4.09 and 4.02 ppm) appeared shifted upfield in the azide (3.35 and 3.25 ppm).



Scheme 2.

Table 1
^{1}H NMR data for compounds **5–14**

	δ (ppm)							*J* (Hz)									
Comp.	**H-1**	**H-3**	**H-3′**	**H-4**	**H-4′**	**H-5**	**H-6,6′**	$J_{3,3'}$	$J_{3,4}$	$J_{3,4'}$	$J_{3',4}$	$J_{3',4'}$	$J_{4,5}$	$J_{4',5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
5	4.98	6.19		6.98		4.67	3.87, 3.78		10.6				1.6		4.2	5.5	11.6
6	4.80	2.89	2.78	3.94		4.36	3.94, 3.80	15.0	3.4		3.1		~1		6.2	4.8	11.5
7	4.70	2.82	2.34	2.14-1.78		4.45	4.17, 4.11	14.9	6.7	13.2	3.2	4.8	2.8	11.2	3.8	6.0	11.8
8	4.73	2.82	2.39	2.08-1.83		4.33	3.70, 3.59	14.9	7.6	12.4	3.2	4.7	2.3	11.3	3.6	6.2	11.6
9	4.64	2.77	2.37	2.06	1.84	4.45	4.09, 4.02	14.9	6.6	13.2	2.6	4.9	2.7	11.3	5.5	4.7	10.6
10	4.74	2.81	2.39	2.09-1.81		4.42	3.35, 3.25	14.8	6.9	13.1	2.7	4.7	3.2	11.1	6.7	4.0	12.9
11	5.12	2.24	1.83-1.68		1.61	4.28	3.31, 3.20	14.8	6.0	13.4		5.0	3.7	11.5	6.9	4.0	12.8
12	6.02	2.59	2.39	1.80	1.66	4.23	3.31, 3.18	14.6	5.6	13.1	2.6	4.6	3.4	11.3	7.0	3.9	12.8
13[a]	5.32	2.41	1.89-1.76		1.65	4.30	3.32, 3.23	14.8	6.0	13.2		4.5		11.3	7.0	4.0	12.8
14[b]	4.72	1.72	1.63-1.56		1.40	3.81[c]	3.44, 3.05			13.5		4.0		11.9	7.2	3.2	13.8

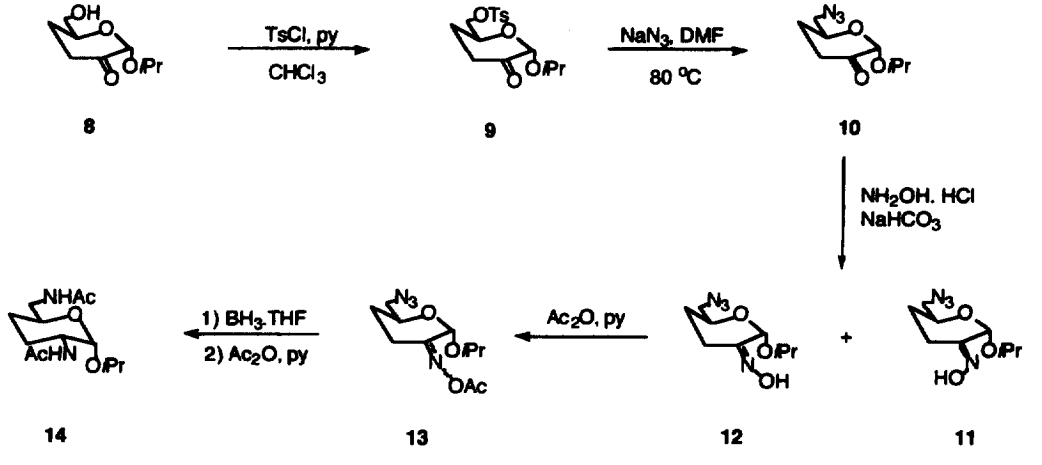
[a] Data for the *E* -isomer [b] In DMSO d_6; H-2 δ 3.96, $J_{1,2}$ 3.4 Hz; $J_{2,3}$ 12.1 Hz; $J_{2,3'}$ 4.0 Hz [c] Overlapped with OC*H*Me$_2$

The reaction of **10** with hydroxylamine hydrochloride in the presence of sodium hydrogen carbonate led to two products which had different mobility by TLC (R_f 0.45 and 0.31; toluene:EtOAc=9:1). This fact indicated that, as expected for non-symmetrical ketones, a diastereoisomeric (*syn, anti*) mixture of ketoximes had been obtained. The mixture was separated by column chromatography, and each compound was individually characterized. The ^{1}H and ^{13}C NMR spectra of both products showed a pattern consistent with that of an oxime structure. The absolute configuration was established taking into account the shift in the resonances of the carbons α to the imine group. These shifts are associated with the conversion of a ketone into its oxime, with the effect for the α-*syn* carbon being greater than for the α-*anti* carbon.[19] With the aid of this correlation, it was easy to assign as the *E* (*anti*)-oxime (**11**), the compound which eluted first from the column. Thus, the signals of C-1 and C-3, when compared with

Table 2
^{13}C NMR data for compounds **5–14**

	δ (ppm)							
Comp.	C-1	C-2	C-3	C-4	C-5	C-6	$OCHMe_2$	$OCH(CH_3)_2$
5	96.2	189.0	126.3	148.1	69.2	64.2	71.7	23.0, 21.7
6	97.6	200.0	38.7	76.3	70.6	62.2	71.3	23.3, 21.6
7	98.0	201.9	34.7	29.2	66.2*	65.7*	71.2	23.3, 21.8
8	97.8	202.9	34.7	28.7	68.8*	64.8*	70.8	23.3, 21.6
9	97.7	201.7	34.3	28.8	65.8	71.0*	70.8*	23.2, 21.5
10	97.7	202.0	34.6	30.1	67.6	54.2	70.9	23.2, 21.6
11	95.3	154.7	18.3	27.7	68.4*	54.7	69.3*	23.2, 21.5
12	88.0	153.8	25.2	29.0	68.2	54.7	70.1	23.2, 21.6
13	94.9	161.1	19.5	28.0	68.1	54.3	70.3	23.1, 21.6
14	95.4	47.6	27.4*	24.3*	67.8	43.4	69.6	23.3, 21.8

*Signals may be interchanged.



8 **9** **10** **14** **13** **12** **11**

Scheme 3.

the resonances of the same carbons in **10**, showed a shifting of 2.4 and 16.3 ppm, indicating that C-3 is *syn* to the N–OH group, and C-1 is *anti*. Consistent with this assignment, the other oxime (**12**) had the *Z*-configuration, according to the same rule.

On standing in a chloroform solution, the *Z*-isomer (**12**) progressively converts into the *E*-isomer (**11**), probably due to the lower steric hindrance of the OH group *syn* to the least substituted α-carbon (C-3). For ketoximes where two isomers may be expected, the major isomer is that of the *anti* configuration.[19]

Various reagents and reaction conditions were employed for the reduction of oximes to amines. Hydrogenolysis of the mixture of **11** and **12** in the presence of Pd or Pt catalysts, with different solvents, concentrations and pressures, gave extremely poor yields of the diamine. Also, reduction with lithium aluminun hydride or Raney nickel proved to be unsuccesful. Borane has been described as a good reducing agent for the preparation of amines from oximes[20] at high temperatures. However, the reduction of oxime ethers or oxime esters can be accomplished at room temperature.[20,21] In the sugar field, Danishefsky and Maring[22] performed the borane reduction of a ketoxime acetate into amine. Therefore,

the mixture of oximes **11** and **12** was acetylated under standard conditions and the acetyl derivative **13** was treated with an excess of borane in THF. We expected that the azide function would be also reduced to amine under those conditions.[23] According to our expectations, after acetylation of the reduction product, the *N,N'*-diacetylpurpurosamine derivative **14** was obtained. The ^{1}H NMR spectrum of **14** showed the signals of two N*H* protons at 5.85 and 5.56 ppm and the singlets of two CH_3 acetyl groups, which dictates that both the azido and the oxime have been reduced. The stereochemistry at C-2 was established on the basis of $J_{1,2}$, $J_{2,3eq}$ and $J_{2,3ax}$ (3.4, 4.0 and 12.1 Hz, respectively) that clearly showed that the amino group was equatorially oriented. The remarkable diastereoselectivity observed for the saturation of the imine double bond may be attributed to the steric hindrance of the quasiaxially disposed vicinal anomeric isopropyl group, which blocks the α-face and induces the attack of borane from the opposite side. We have previously observed similar anomeric stereocontrol in the reduction of a vicinal carbonyl group.[24]

In summary, a simple and direct synthesis of purpurosamine C derivative **14** has been accomplished using readily available reagents, in an overall yield of ~40% (from 2-acetoxy-3,4,6-tri-*O*-acetyl-D-galactal). Some key features of the synthesis are:

(i) the chiral template for the synthesis of **14**, the dideoxyhex-2-ulose **7**, was readily prepared from per-*O*-acetyl-D-galactose by a high yielding, three-step procedure;
(ii) the nitrogen containing groups (azide and oxime) were easily introduced in the molecule of **7** by direct functional group transformations and with excellent yields; and
(iii) the reduction of the azide and the oxime was performed in a single, highly diastereoselective step, to afford the purpurosamine C derivative **14**.

3. Experimental

3.1. General

Solvents were dried and purified by appropriate standard procedures. TLC was performed on aluminun plates precoated with silica gel 60 F_{254} (Merck), developed with the solvents indicated in each individual case. The spots were visualized by exposure to UV light and by heating after immersion in a solution of *p*-anisaldehyde (0.5% v/v) in ethanol containing 5% H_2SO_4. Column chromatography was performed with silica gel 60 (200–400 mesh, Merck). Optical rotations were measured with a Perkin–Elmer 343 polarimeter. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC 200 (^{1}H: 200 MHz, ^{13}C: 50.3 MHz) or a Bruker 500 (^{1}H: 500 MHz) spectrometer in $CDCl_3$ with TMS as an internal standard unless otherwise stated. Melting points are uncorrected and were determined on a Fisher–Johns apparatus. Mass spectral data, electron impact mass spectra (EIMS) and FAB+, were obtained on a Shimadzu QP5000 spectrometer opperating at 70 eV, and a ZAB-SEQ4F spectrometer, respectively.

3.2. *2-Acetoxy-3,4,6-tri-*O*-acetyl-*D*-galactal (3) and isopropyl 6-*O*-acetyl-3,4-dideoxy-α-*D*-glycero-hex-3-enopyranosid-2-ulose (4)*

Compound **3** was prepared from per-*O*-acetyl-D-galactose as previously described.[16] Treatment of **3** with 2-propanol in the presence of tin(IV) chloride afforded **4** (90% yield).[15]

3.3. *Isopropyl 3,4-dideoxy-α-D-glycero-hex-3-enopyranosid-2-ulose (5) and isopropyl 3-deoxy-4-O-methyl-α-D-threo-hexopyranosid-2-ulose (6)*

To an externally cooled (0°C) and stirred solution of **4** (121 mg, 0.54 mmol) in anhydrous methanol (30 mL) was added 0.5 M NaOMe (1 mL) under N_2. After 1 h of stirring, TLC showed complete transformation of the starting material into two lower moving compounds having R_f 0.29 and 0.19 (toluene:EtOAc=2:1). The solution was neutralized by addition of Dowex 50W (H^+). The resin was filtered and the filtrate was concentrated to a syrup, which was chromatographed on a silica gel column with toluene:EtOAc (5:1) as eluent. The 2-ulose **5** (31 mg, 31%) was isolated from the fractions of R_f 0.29. EIMS, m/z: 155 ($M^{+\cdot}-CH_2OH^{\cdot}$, 1%), 127 ($M^{+\cdot}-OiPr^{\cdot}$, 3%), 114 (3%), 113 (4%), 98 (54%), 97 (38%), 85 (9%), 81 (9%), 70 (41%), 55 (20%), 42 (100%). FAB, m/z: 187 (M+1).

The more polar product was identified as a 9:1 mixture of **6** and its *erythro* isomer (48 mg, 42%). EIMS, m/z: 190 ($M^{+\cdot}-CO^{\cdot}$, 1%), 175 ($M^{+\cdot}-iPr^{\cdot}$, 1%), 159 ($M^{+\cdot}-OiPr^{\cdot}$, 11%), 130 (27%), 115 (7%), 99 (7%), 97 (7%), 89 (8%), 87 (12%), 84 (11%), 71 (100%), 61 (37%), 58 (33%), 57 (23%), 55 (11%), 45 (24%). FAB, m/z: 219 (M+1).

3.4. *Isopropyl 3,4-dideoxy-α-D-glycero-hexopyranosid-2-ulose (8)*

To a stirred solution of **7**[24] (0.54 g, 2.3 mmol) in anhydrous methanol (21 mL) was added 0.5 M NaOMe (2 mL) in an N_2 atmosphere. After 3 h of stirring at room temperature the solution was neutralized by addition of Dowex 50W (H^+). The resin was filtered and the solvent evaporated to give a syrup, which was chromatographed using toluene:EtOAc (3:1) to afford pure compound **8** (0.43 g, 97%); $[\alpha]_D$=+128 (*c* 0.87, $CHCl_3$). Anal. calcd for $C_9H_{16}O_4$: C, 57.41; H, 8.57. Found: C, 57.30; H, 8.74.

3.5. *Isopropyl 6-O-(p-tolylsulfonyl)-3,4-dideoxy-α-D-glycero-hexopyranosid-2-ulose (9)*

To a stirred solution of crude **8** (0.45 g, 2.37 mmol) in dry $CHCl_3$ (4.2 mL), externally cooled at 0°C, were added pyridine (0.38 mL, 4.7 mmol) and tosyl chloride (0.7 g, 3.5 mmol). After stirring at room temperature for 16 h, water (6 mL) was added, and the stirring was maintained for 0.5 h. The mixture was diluted with CH_2Cl_2 and it was successively washed with 2 N aqueous HCl, saturated aqueous $NaHCO_3$, and water. The organic extract was dried ($MgSO_4$) and concentrated. The resulting syrup was purified by column chromatography with CH_2Cl_2 as eluent, to afford pure **9** (0.63 g, 94%); $[\alpha]_D$=+63 (*c* 0.98, $CHCl_3$). Anal. calcd for $C_{16}H_{22}O_6S$: C, 56.12; H, 6.48. Found: C, 56.35; H, 6.62.

3.6. *Isopropyl 6-azido-3,4,6-trideoxy-α-D-glycero-hexopyranosid-2-ulose (10)*

Compound **9** (0.28 g, 0.82 mmol) was dissolved in anhydrous DMF (5 mL) and sodium azide (0.15 g, 2.3 mmol) was added. The resulting suspension was heated with stirring at 80°C for 18 h under N_2, at which time TLC showed a main spot having R_f 0.38 (hexane:EtOAc=10:1) and no starting material remaining. The reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic extract was dried ($MgSO_4$) and concentrated to a syrup, which was chromatographed using toluene:EtOAc (14:1) as eluent. Compound **10** (0.14 g, 82%) was obtained as an oil; $[\alpha]_D$=+74 (*c* 0.81, $CHCl_3$). Anal. calcd for $C_9H_{15}O_3N_3$: C, 50.68; H, 7.09; N, 19.71. Found: C, 50.67; H, 6.76; N, 19.86.

3.7. *Isopropyl 6-azido-3,4,6-trideoxy-α-D-glycero-hexopyranosid-2-ulose* E- *and* Z-*oximes (11 and 12)*

To a solution of **10** (96 mg, 0.45 mmol) in anhydrous isopropyl alcohol (2 mL), hydroxylamine hydrochloride (68 mg, 0.9 mmol) and $NaHCO_3$ (72 mg, 0.87 mmol) were added, and the mixture was stirred at room temperature for 1 h. TLC showed the complete transformation of the starting material into two lower moving compounds having R_f 0.45 and 0.31 (toluene:EtOAc=9:1). The salts were filtered and the solvent was evaporated to a syrup, which was chromatographed on a silica gel column with toluene:EtOAc (10:1). The less polar product was characterized as the oxime having the *E*-configuration (**11**, 56 mg, 55%); $[\alpha]_D$=+106 (*c* 0.70, $CHCl_3$). Anal. calcd for $C_9H_{16}O_3N_4$: C, 47.34; H, 7.07; N, 24.55. Found: C, 47.55; H, 7.21; N, 24.21. From the fractions of R_f 0.31 was isolated the *Z*-oxime (**12**, 40 mg, 39%), which converts into the *E*-isomer on standing.

3.8. *Isopropyl 6-azido-3,4,6-trideoxy-α-D-glycero-hexopyranosid-2-ulose* E,Z-*oxime acetate (13)*

The crude mixture of oximes obtained as described above from **10** (84 mg, 0.39 mmol) was dissolved in pyridine (1 mL) and cooled to 0°C. Acetic anhydride was added (1 mL) and the mixture was stirred for 1 h. The solvents were evaporated by co-distillation with MeOH and toluene, and the residue was chromatographed (toluene:EtOAc=15:1) to give a ~7:1 mixture of the *E*/*Z* oxime acetates (**12**, 102 mg, 96%). EIMS, m/z: 211 ($M^{+\cdot}-O\dot{i}Pr$, 2%), 169 (25%), 113 (9%), 95 (9%), 84 (5%), 78 (4%), 68 (26%), 55 (16%), 43 (100%). FAB, m/z: 271 (M+1).

3.9. *Isopropyl 2,6-*N,N*-diacetamido-2,3,4,6-tetradeoxy-α-D-erythro-hexopyranoside (14)*

To a solution of compound **13** (101 mg, 0.37 mmol) in anhydrous THF (1.5 mL) cooled at −18°C, 2.5 M solution of $BH_3 \cdot THF$ (1.2 mL, 3 mmol) was added. The mixture was stirred for 3 h at −18°C, and then at room temperature for an additional 18 h. Methanol (3 mL) was added to decompose the excess of borane, and the solvents were evaporated. The residue was dissolved in trifluoroacetic acid (0.9 mL) and the solution was stirred for 0.5 h at room temperature. TFA was evaporated, and the residue was dissolved in pyridine (1 mL) and cooled to 0°C. Acetic anhydride (1 mL) was added, and the reaction mixture was stirred at room temperature for 20 h. After evaporation of the solvents, the resulting syrup was chromatographed using EtOAc to afford crystalline **14** (66 mg, 65%). After recrystallization from acetone, **14** had m.p. 195–196°C; $[\alpha]_D$=+113 (*c* 0.71, $CHCl_3$). Anal. calcd for $C_{13}H_{24}O_4N_2$: C, 57.37; H, 8.88; N, 10.29. Found: C, 57.29; H, 9.04; N, 10.12.

Acknowledgements

We are indebted to UMYMFOR (FCEN-CONICET) for the microanalyses. Financial support from the Universidad de Buenos Aires (Project EX 173), Fundación Antorchas and the National Research Council of República Argentina (CONICET) is gratefully acknowledged. O.V. is a Research Member of CONICET.

References

1. Umezawa, S. *Adv. Carbohydr. Chem. Biochem.* **1974**, *30*, 111.
2. Kuwahara, R.; Tsuchiya, T. *Carbohydr. Res.* **1997**, *299*, 271.

3. Kondo, S.; Iinuma, K.; Yamamoto, H.; Maeda, K.; Umezawa, H. *J. Antibiot.* **1973**, *26*, 412.
4. (a) Guthrie, R. D.; Williams, G. J. *Chem. Commun.* **1971**, 923. (b) Guthrie, R. D.; Williams, G. J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2619.
5. (a) Cleophax, J.; Leboul, J.; Olesker, A.; Gero, S. D. *Tetrahedron Lett.* **1973**, 4911. (b) Cleophax, J.; Gero, S. D.; Jegou-Aumont, E.; Leboul, J.; Mercier, D. *J. Chem. Soc., Chem. Commun.* **1975**, 11.
6. Brimacombe, J. S.; Da'aboul, I.; Tucker, L. C. N. *J. Chem. Soc., Perkin Trans. 1* **1975**, 979.
7. Cleophax, J.; Olesker, A.; Rolland, A.; Gero, S. D.; Forchioni, A. *Tetrahedron* **1977**, *33*, 1303.
8. Brimacombe, J. S.; Hunedy, F.; Mather, A. M.; Tucker, L. C. N. *Carbohydr. Res.* **1979**, *68*, 231.
9. Ohashi, Y.; Okuno, S.; Takeda, K.; Ito, Y. *Carbohydr. Res.* **1978**, *67*, 503.
10. Liang, X.; Krieger, R.; Prinzbach, H. *Tetrahedron Lett.* **1995**, *36*, 6433.
11. Brimacombe, J. S.; Da'aboul, I.; Tucker, L. C. N. *J. Chem. Soc., Perkin Trans. 1* **1974**, 263.
12. Golebiowski, A.; Jacobsson, U.; Chmielewski, M.; Jurczak, J. *Tetrahedron* **1987**, *43*, 599.
13. Bauer, T.; Jezewski, A.; Jurczak, J. *Tetrahedron: Asymmetry* **1996**, *7*, 1405.
14. David, S.; Lubineau, A.; Gero, S. D. *J. Org. Chem.* **1979**, *44*, 4986.
15. Varela, O.; De Fina, G. M.; de Lederkremer, R. M. *Synthesis* **1988**, 891.
16. Varela, O.; De Fina, G. M.; de Lederkremer, R. M. *Carbohydr. Res.* **1987**, *167*, 187.
17. Ferrier, R. J. *Adv. Carbohydr. Chem. Biochem.* **1969**, *24*, 199.
18. Perlin, C. L. *Tetrahedron* **1995**, *51*, 11901.
19. Hawkes, G. E.; Herwig, K.; Roberts, J. D. *J. Org. Chem.* **1974**, *39*, 1017.
20. Feuer, H.; Braunstein, D. M. *J. Org. Chem.* **1969**, *34*, 1817.
21. Hassner, A.; Catsoulacos, P. *Chem. Commun.* **1967**, 590.
22. Danishefsky, S. J.; Maring, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 1269.
23. Hassner, A.; Levy, L. A. *J. Am. Chem. Soc.* **1965**, *87*, 4203.
24. De Fina, G.; Varela, O.; de Lederkremer, R. M. *Carbohydr. Res.* **1993**, *246*, 1993.