Pergamon

Tetrahedron: Asymmetry, Vol. 8, No. 20, pp. 3443–3456, 1997

Printed in Great Britain
PII: S0957-4166(97)00404-7
0957-4166/97 $17.00 + 0.00

Stereoselective syntheses of 4-amino-aldoses, and chiral pyrrolidine derivatives from glycosylenamines

José Fuentes,* David Olano and M. Angeles Pradera

Dpto de Química Orgánica, Facultad de Química, Universidad de Sevilla, Apartado de Correos No 553, E-41071 Sevilla, Spain

Abstract: The stereocontrolled synthesis of *N*-protected 4-amino-4-deoxy-D-*galacto*- and -L-*arabino*-pyranoses starting from glycosylenamines via aza-anhydropyranoses is described. The steroselective transformation of the intermediate aza-anhydropyranoses into chiral pyrrolidines is also reported. © 1997 Elsevier Science Ltd

Introduction

The dialkoxycarbonylvinyl group is a versatile *N*-protecting group[1] that has been employed to protect the amino function of amino sugars[2] and glycosylamines.[3] The corresponding enamino sugars have been used in the stereocontrolled synthesis of glycosyl isothiocyanates,[3,4] deoxyisothiocyanatosugars,[4,5] and *N*-formyl and *N*-acylamino sugars,[6] and in the preparation of selectively *O*-protected amino aldopyranosides and amino alditols.[7] Partially *O*-protected and unprotected dialkoxycarbonylvinylamino aldoses have been employed as glycosyl acceptors in several glycosylation reactions.[3,8–10]

Amino sugars, with the amino group in different positions of the sugar ring, have been synthesised by nucleophilic displacement reactions of sulphonyloxy groups, such as *p*-toluenesulphonates[11,12] or triflates.[13] This displacement has most frequently been intermolecular using nitrogen functional groups as nucleophiles, and in some cases these reactions have been used in an intramolecular way to form five- and six-membered rings in carbohydrate derivatives.[12] At the same time the 4-amino-4-deoxy sugars and their derivatives are interesting compounds from biological and pharmaceutical points of view, as they have been identified as constituents of several natural antibiotics and antifungal agents.[12,14,15] Recently 4-amino-4-deoxy-glucosides have been used in the preparation of 4-guanidinium sugars.[16] These 4-amino compounds are also interesting as synthetic precursors of glycocyanamoylspermidines[17] (a family of broad spectrum antibiotics), sugar isothiocyanates, sugar thioureas,[8,16] and β-lactams.[18]

The chiral pyrrolidines take part in the structure of natural and synthetic antibiotics such as lincomycin, celecticetin, and clindamicin, and particularly those having the typical substituents of the sugars (azafuranoses, and azafuranosides) have been found in the structure of pseudotrisaccharides related with the core region of the antibiotic esperamicin.[19] They are also interesting intermediates in the synthesis of neacine bases from aldoses.[20] Furthermore the azasugars have been used as glycosidase and glycosyl-transferase inhibitors and have several pharmaceutical uses, in the treatments of diabetes melitus,[21] of different inflamations, metastasis and virus infections. Particularly these glycosidase inhibitors have activity against the human immunodeficiency virus (HIV).[22] This activity is higher when the lipophilicity of the azacompound is increased by the presence of a fatty substituent, such as a butyl group, bonded to the nitrogen atom.[23] The synthesis of chiral pyrrolidines (five membered azasugars) is an active topic in chemical research; in the last few years several synthetic strategies starting from erythrose[24] and ribose[20] acetals, arabinofuranose derivatives,[25,26] aminodisaccharides,[27] pentofuranosylamines,[28] and unsaturated heptulose derivatives,[29] have been developed.

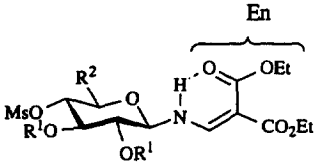
* Corresponding author.

In a preliminary communication[30] we have reported on the formation of 1,4-aza-anhydrosugars from glycopyranosylenamines. In this paper we describe several glycopyranosylenamines **1–4** with suitable substituents for the stereocontrolled formation of the 1,4-aza-anhydroaldose derivatives **5–8**. The cleavage of the C1–N bond of **5–8** leads to the 4-enamino-4-deoxysugars **9–11**. These two reactions constitute a new way to introduce the amino function in the position 4 of the pyranose ring with total control of the stereochemistry. The method provides a valuable alternative to the S_N2 displacement of a sulphonyloxy group by sodium azide and further reduction, because in the latter the elimination reaction competes with the substitution.

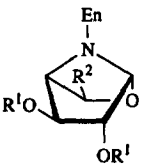
The cleavage of the C1–O bond of **5–8** produces chiral pyrrolidines (azasugars) as sole products **16** and **20** or as pairs of diastereomers **12–15** epimeric at C2 (C1 of the sugar ring). The degree of stereoselection depends on the reaction conditions.

Results and discussion

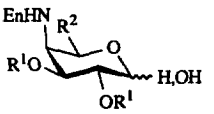
The 4-mesyloxyglycosylenamines **1–4**, having the enamino and the sulphonyloxy groups in a *trans* relationship, in our case with D-*gluco* and D-*lyxo* configurations, were chosen as starting materials. These compounds were prepared by mesylation of suitably protected glycosylamines. The starting material for **1** was 2,3,6-tri-*O*-benzoyl-*N*-(2,2-diethoxycarbonylvinyl)-β-D-glucopyranosylamine,[31] for **2** *N*-(2,2-diethoxycarbonylvinyl)-6-*O*-trityl-β-D-glucopyranosylamine,[32] for **4** *N*-(2,2-diethoxycarbonylvinyl)-β-D-xylopyranosylamine.[33] In the case of compound **3** the treatment of *N*-(2,2-diethoxycarbonylvinyl)-β-D-glucopyranosylamine[33] with a limited amount of acetic anhydride yielded a mixture of the partially protected 2,3,6- and 2,4,6-tri-*O*-acetyl derivatives; which treated with mesyl chloride gave a 1:2 mixture of the corresponding 3-*O*-mesyl and 4-*O*-mesyl (**3**) esters. This was used in the following steps without purification.



1-4



5-8



9-11

	R^1	R^2
1, 5, 9	Bz	CH_2OBz
2, 6	Ms	CH_2OTr
3, 7	Ac	CH_2OAc
4, 8, 11	Ms	H
10	Ms	CH_2OH

The ^1H and ^{13}C NMR (see Table 1 and experimental) spectra of compounds **1**, **2**, and **4** showed the characteristic signals of the enamino group of *N*-diethoxycarbonylvinylglycosylamines,[3] and the chemical shifts for the resonances of H-4 of the sugar ring were in the range 4.68–5.18 in agreement with the presence of an ester group in this position.[31]

The treatment of **1–4** with one equivalent of sodium methoxide in hexamethylphosphoramide (HMPT) gave the 1,4-aza-anhydropyranoses **5–8** in high yields. The ^1H NMR spectra of **5–8** (Table 1) had no signals for NH and showed a singlet for the *HC*= of the enamino moiety (=$CHNR_2$) instead of the doublet (=CHNHR) of the spectra of **1–4**. The signals for H-1 were strongly downfield shifted (≈1.1 ppm) whereas the resonances for H-4 were upfield shifted as corresponds to the substitution of the ester group by an enamino group. Other differences observed in the ^1H NMR spectra were changes in the chemical shifts of *HC*=, and very strong changes in all the coupling constants of the sugar ring, which were in accord with the expected values for the boat conformation. Additionally in the case of **7** a ^4J W coupling constant (0.8 Hz) between H-1 and H-3 was observed. The chemical

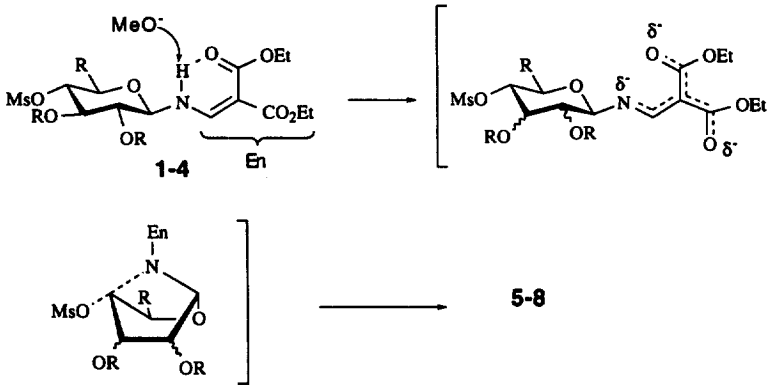
Table 1. Relevant NMR data (δ, ppm; *J*, Hz) for compounds **1**, **2**, **4**–**11**

	Sugar Ring							Enamino moiety				
	δH-1	$J_{1,2}$	δH-4	$J_{3,4}$	$J_{4,5}$	δC-1	δC-4	δN-H	$J_{1,NH}$[a]	δC*H*	δ=*C*H	δ=C
1	4.82t	9.4	5.18t	9.4	9.4	87.4	73.5	9.37dd	9.4	7.94d	157.0	95.3
2	4.60t	9.0	4.99t	9.0	9.0	86.3	73.6	9.45dd	9.0	8.00d	156.8	95.5
4	4.56t	9.1	4.77-4.68m	9.2	5.7 10.8	87.1	76.3	9.34dd	9.1	7.96d	157.0	95.7
5	5.90d	2.1	4.95bs	-	-	88.5	64.7	-	-	7.76s	145.3	100.3
6	5.63d	2.5	4.64s	-	-	86.9	66.5	-	-	7.37s	145.5	101.4
7	5.63dd	2.4	4.57s	-	-	88.1	64.0	-	-	7.62s	145.5	100.1
8	5.60d	2.6	4.68d	-	3.7 0.0	88.0	64.9	-	-	7.46s	144.8	104.8
9[b]	5.84d	3.3	4.15dd	3.9	0.0	90.7	59.4	9.74dd	9.6	7.88d	159.8	91.9
10[b]	5.54d	3.8	4.29-4.11m	4.1	0.0	90.6	59.4	9.39dd	9.5	8.10d	160.5	91.6
11[b]	5.59d	3.5	4.04ddd	4.1	2.0 0.0	91.2	58.4	9.52-9.42m	8.8	8.12d	159.6	92.0

[a] $J_{4,NH}$ for **9**-**11**. [b] Data for the α anomer.

shifts of the resonances of C-1 in **5**–**8** showed small changes when they were compared with the same signals for **1**–**4**, but the resonances of C-4 were upfield shifted 7.1–11.4 ppm (change of C–O by C–N). Important shifts were also observed in the signals corresponding to the resonances of the carbons of the enamino moiety (see Table 1).

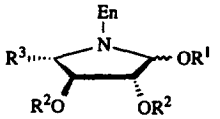
The formation of **5**–**8** probably takes place through a stabilised intermediate ion which is formed by attack of the methoxide ion on the NH group. The intermediate ion produces the nucleophilic intramolecular displacement of the mesyloxy group (Scheme 1). A related nucleophile-induced rearrangement involving the sulphur atom of thioglycosides has recently been described.[34]



Scheme 1.

Reaction of **5**, **6**, and **8** with trifluoroacetic acid:water 3:1 yielded **9**–**11** respectively as mixtures of α and β anomers. In the case of **6** detritylation tooks place. The anomeric carbons of these compounds resonated at lower field than the same nuclei in **1**–**8**, whereas the signals for H-4 and C-4 were shifted upfield with respect to the corresponding signals in **1**–**8**. The spectra of compounds **9**–**11** showed signals for NH and the resonances for the enamino moieties had similar couplings to those for **1**, **2**, and **4**. The $J_{4,5}$ value in **9** and **10** was ≈0.0 Hz as it is described for related D-galactopyranosyl derivatives.[8,31]

The chiral pyrrolidines with an alkyl chain on the nitrogen atom **12–21** were obtained by cleavage of the C1–O bond of **5–8**. When this cleavage was performed using acetic anhydride and trimethylsilyltrifluoromethane sulfonate in the same way as described[35] for 1,6 anhydrosugars the 2-acetoxy derivatives **12–15** were formed as mixtures of 2*R* and 2*S* diastereomers. Digital integration of the ^{1}H NMR signals showed no or low stereoselectivity (*R/S* ratio 1:1 to 1:3). However when the reaction was carried out with methanol in the presence of lithium perchlorate and after trifluoroacetic acid–trifluoroacetic anhydride the stereoselectivity was 100% and only the *2S* diastereomer was obtained. Thus starting from **5, 6,** and **8** the pyrrolidine **16, 18** (which evolved to **22**), and **20** were obtained. Acetylation of **16** and **20** gave **17** and **21** respectively. In the cases of the reactions starting from **6** and **8** addition of the OH group on the double bond of the enamino radical took place and the bicyclic compounds **22** and **23** were formed as a main (from **6**) or minor (from **8**) product.



	R^1	R^2	R^3	Conf. C-2
12	Ac	Bz	OAc, OBz	R and S
13	Ac	Ms	OAc, OAc	R and S
14	Ac	Ac	OAc, OAc	R and S
15	Ac	Ms	CH_2OAc	R and S
16	Me	Bz	OH, OBz	S
17	Me	Bz	OAc, OBz	S
18[a]	Me	Ms	OH, OTr	S
19[a]	Me	Ms	OH, OH	S
20	Me	Ms	CH_2OH	S
21	Me	Ms	CH_2OAc	S

[a]Isolated as traces.

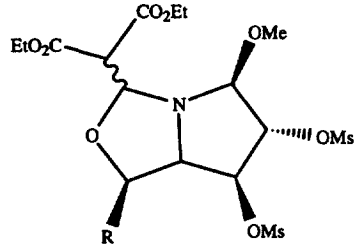
The diastereomeric mixtures **12–15** and compounds **16–23** were amorphous solids of easy decomposition and their structures were based on HRMS, IR, and ^{1}H and ^{13}C NMR spectroscopic data (see Table 2 and experimental). The chemical shifts for the resonances of H-2 and C-2 in **12–15** were in agreement with those expected for a CH group simultaneously joined to oxygen (OAc) and nitrogen atoms, whereas the δ values for the resonances of H-5 and C-5, close to those for H-4 and C-4 in **5–11**, supported the idea that the C5–N bond is not affected during the reaction. The configuration of C-2 was

Table 2. Relevant NMR data (δ, ppm; *J*, Hz) for **12–21**[36]

	Conf. C-2	δH-2	δH-5	$J_{2,3}$	δC-2	δC-5	δN-C*H*	δN-C*H*
12	R	6.58d	4.30-4.10m	5.2	84.7	61.1	7.60s	145.5
	S	6.45s	4.27-4.08m	0.0	86.9	61.1	7.71s	146.1
13	R	6.32d	4.51m	5.1	85.6	62.0-60.9	7.45s	145.3
	S	6.16s	4.41m	0.0	83.7	62.0-60.9	7.41s	145.3
14	R	6.30d	4.64m	5.3	87.2	62.1	7.48s	144.7
	S	6.19s	4.58m	0.0	87.2	62.1	7.63s	144.6
15	R	6.45d	4.51-4.15m	4.7	82.5	61.9-59.9	7.53s	143.7
	S	6.36s	4.51-4.15m	0.0	83.1	61.9-59.9	7.52s	143.3
16	S	5.23s	4.24-4.14m	0.0	93.5	60.8	7.71s	147.3
17	S	5.14s	4.25-4.11m	0.0	92.6	60.5	7.59s	146.5
20	S	5.12s	4.20m	0.0	94.2	60.9	7.50s	145.4
21	S	5.00s	4.36-4.28m	0.0	93.5	61.1	7.47s	145.3

supported by the $J_{2,3}$ value, which was in the range 4.7–5.1 Hz for *R* isomers (*cis* relationship between H-2 and H-3), and was close to 0 Hz for *S* isomers (*trans* relationship between the same protons) in accord with reported data on coupling constans values for related pyrrolidine[28] and tetrahydrofuran[37] rings. The NMR data of the crude reaction products starting from **5**, **6**, and **8** in the presence of lithium perchlorate showed no signals for the 2*R* isomers and the spectra of the isolated pyrrolidines (**16** and **20**) and of the acetyl derivatives (**17** and **21**) were similar to those for the 2*S* isomers of **12–15** with the expected changes in the chemical shifts of H-2 and C-2.

The spectroscopic data of **22** and **23** supported the fused rings bicyclic structure. The NMR data did not show significant signals for a second compound, but the configuration of the stereogenic center C-2, formed in the addition of the OH on the enamine double bond, could not be assigned. The resonance of C-2 appeared close to that for C-8 and both chemical shifts (91.2 and 88.0 ppm respectively) supported carbon atoms simultaneously joined to oxygen and nitrogen atoms. Compounds **22** and **23** are 3-oxo analogues of polyhydroxy pyrrolizidine alkaloids which exhibit interesting biological activities.[38]



22 R= CH_2OH
23 R=H

The stereoselectivity (C-2) in the formation of **16**, **18**, and **20** probably originates because the lithium atom is situated between the nitrogen and the oxygen ring atoms in the aza-anhydrosugar **5**, **6**, or **8** and then the methanol molecule attacks on the opposite face.

In conclusion we have described the high yielding formation of aza-anhydrosugars **5–8** from glycosylenamines **1–4**. These azasugars can be used in the stereocontrolled preparation of *N*-protected 4-amino sugars **9–11**, and in the formation of chiral pyrrolidines **12–23** in some cases with total stereoselectivity. The method is limited to glycosylenamines with a 4-mesyloxy group in *trans* relationship with the enamino group, and in the case of pentose derivatives give access to 4-amino sugars of the L-series.

The enamino group is easy to remove under mild conditions.[3]

Experimental

General

Melting points are uncorrected. Optical rotations were measured at 19–28°C for solutions in dichloromethane. FTIR spectra were recorded for KBr discs or thin film. ^{1}H NMR spectra (300, 500 MHz) were obtained for solutions in $CDCl_3$. Assignments were confirmed by homonuclear 2D COSY correlated experiments. ^{13}C NMR spectra were recorded at 75.4, 125.7 MHz. Heteronuclear 2D correlated spectra were obtained in order to assist in carbon resonance assignments. Mass spectra (EI and FAB) were recorded with a Kratos MS-80RFA instrument with a resolution of 1000 or 10000 (10% valley definition). For the FAB spectra ions were produced by a beam of xenon atoms (6–7 KeV) using 3-nitrobenzyl alcohol and thioglycerol as matrix and NaI as salt. TLC was performed on Silica Gel HF_{254}, with detection by UV light or charring with H_2SO_4. Silica Gel 60 (Merck, 70–230 and 230–400 mesh) was used for preparative chromatography.

General procedure for the preparation of 1–4

To a stirred solution of the corresponding glycopyranosylenamine (0.45 mmol) in pyridine (x mL) at 0°C was gradually added methylsulphonyl chloride (y mL, z mmol). The mixture was kept at r.t. for t h. The reaction was controlled by TLC until total consumption of the starting material. Compounds **1** and **2** were poured into ice–water and then filtered as white solids. The reaction mixture for **3** and **4** was added into ice–water and then extracted with chloroform (3×10 mL), the organic layer was separated, washed with 1 M sulphuric acid (3×10 mL), saturated aqueous sodium hydrogencarbonate (3×10 mL), and water (3×10 mL), dried ($MgSO_4$), and concentrated to dryness, and the residue was purified as indicated.

*2,3,6-Tri-*O*-benzoyl-*N*-(2,2-diethoxycarbonylvinyl)-4-*O*-mesyl-β-*D*-glucopyranosylamine 1*

From 2,3,6-tri-*O*-benzoyl-*N*-(2,2-diethoxycarbonylvinyl)-β-D-glucopyranosylamine.[31] x=13.5 mL; y=0.1 mL; z=1.13 mmol; t=24 h; TLC eluant ether:hexane 4:1. The residue was crystallized from ether to give 0.325 g (97%); mp. 146–148°C; $[\alpha]_D^{28}$ −18 (*c* 1.0); IR ν_{max} 3285, 2980, 2940, 1724, 1661, 1611, 1452, 1350, 1267, 1179, 1090, 957, 829, and 710 cm^{-1}; ^{1}H NMR: Table 1 and δ 9.37 (dd, 1 H, $J_{NH,=CH}$=13.1, NH), 8.14–7.26 (m, 15 H, 3 Ph), 7.94 (d, 1 H, HC=), 5.91 (t, 1 H, $J_{2,3}$=9.4, H-3), 5.50 (t, 1 H, H-2), 4.78 (dd, 1 H, $J_{6a,6b}$=12.6, $J_{5,6a}$=1.9, H-6a), 4.60 (dd, 1 H, $J_{5,6b}$=4.1, H-6b), 4.25, 4.14 (each m, each 2 H, 2 CH_2CH_3), 4.12–4.09 (m, 1 H, H-5), 2.75 (s, 3 H, Ms), 1.31, 1.23 (each t, each 3 H, $^3J_{H,H}$=7.1, 2 CH_2CH_3); ^{13}C NMR: Table 1 and δ 167.3 (C=O chelated), 166.0 (C=O free), 165.5, 165.3, 165.2 (each 1 C, 3 C=O of Bz), 157.0 (HC=), 133.7–128.0 (18 C, 3 Ph), 95.3 (C=), 74.0 (C-5), 72.0 (C-3), 71.0 (C-2), 61.9 (C-6), 60.3, 60.0 (each 1 C, 2 CH_2CH_3), 38.8 (Ms), 14.2, 14.1 (each 1 C, 2 CH_2CH_3); FABMS *m/z* 762 ([M+Na]$^{+\cdot}$), 740 ([M+H]$^{+\cdot}$), 694 ([M-OEt]$^{+\cdot}$). Anal. Calcd for $C_{36}H_{37}NO_{14}S$: C, 58.45; H, 5.04; N, 1.89; S, 4.33. Found: C, 58.43; H, 5.05; N, 2.03; S, 4.66.

N-*(2,2-Diethoxycarbonylvinyl)-2,3,4-tri-*O*-mesyl-6-*O*-trityl-β-*D*-glucopyranosylamine 2*

From *N*-(2,2-diethoxycarbonylvinyl)-6-*O*-trityl-β-D-glucopyranosylamine.[32] x=1 mL; y=0.29 mL; z=3.14 mmol; t=16 h; TLC eluant ethyl acetate:hexane 6:1. The residue was crystallized from ether to give 0.306 g (82%); m.p. 196–198°C; $[\alpha]_D^{24}$ +22 (*c* 1.0); IR ν_{max} 3036, 2982, 2940, 1707, 1661, 1611, 1451, 1354, 1244, 1177, 1038, 955, 812, and 706 cm^{-1}; ^{1}H NMR: Table 1 and δ 9.45 (dd, 1 H, $J_{NH,=CH}$=13.0, NH), 8.00 (d, 1 H, HC=), 7.43–7.22 (m, 15 H, 3 Ph), 4.94 (t, 1 H, $J_{2,3}$=9.0, H-3), 4.75 (t, 1 H, H-2), 3.70 (dd, 1 H, $J_{6a,6b}$=11.2, $J_{5,6a}$=1.9, H-6a), 3.67 (ddd, 1 H, $J_{5,6b}$=3.8, H-5), 3.38 (dd, 1 H, H-6b), 4.31 (m, 2 H, CH_2CH_3), 4.19 (q, 2 H, $^3J_{H,H}$=7.1, CH_2CH_3), 3.27, 3.15, 2.79 (each s, each 3 H, 3 Ms), 1.35, 1.23 (each t, each 3 H, 2 CH_2CH_3); ^{13}C NMR: Table 1 and δ 167.6 (C=O chelated), 165.0 (C=O free), 156.8 (=CH), 142.8–127.2 (18 C, 3 Ph), 95.5 (C=), 87.4 (CPh_3), 77.5 (C-3), 76.4 (C-2), 74.8 (C-5), 61.6 (C-6), 60.4, 60.1 (each 1 C, 2 CH_2CH_3), 39.4, 39.3, 38.6 (each 1

C, 3 Ms), 14.1 (2 C, 2 CH_2CH_3); FABMS *m/z* 848 ([M+Na]$^{+\cdot}$). Anal. Calcd for $C_{36}H_{43}NO_{14}S_3$: C, 53.38; H, 5.35; N, 1.73; S, 11.88. Found: C, 53.27; H, 5.19; N, 1.79; S, 11.73.

*2,3,6-Tri-*O*-acetyl-*N*-(2,2-diethoxycarbonylvinyl)-4-*O*-mesyl-β-*D*-glucopyranosylamine **3** and 2,4,6-tri-*O*-acetyl-*N*-(2,2-diethoxycarbonylvinyl)-3-*O*-mesyl-β-*D*-glucopyranosylamine*

The starting material was *N*-(2,2-diethoxycarbonylvinyl)-β-D-glucopyranosylamine[33] (0.94 mmol) which was acetylated with acetic anhydride (0.27 ml) and pyridine (2.77 ml) to give a 1:2 mixture (0.214 g) of 2,3,6-tri-*O*-acetyl-*N*-(2,2-diethoxycarbonylvinyl)-β-D-glucopyranosylamine and 2,4,6-tri-*O*-acetyl-*N*-(2,2-diethoxycarbonylvinyl)-β-D-glucopyranosylamine that was treated as described above. x=9.5 mL; y=0.11 mL; z=1.19 mmol; t=10.5 h; column chromatography (ether:hexane 12:1) of the residue gave an amorphous solid which was a 1:2 mixture of **3** and 2,4,6-tri-*O*-acetyl-*N*-(2,2-diethoxycarbonylvinyl)-3-*O*-mesyl-β-D-glucopyranosylamine (0.189 g, 76%). This mixture was directly used in the following step (→**7**).

*N-(2,2-Diethoxycarbonylvinyl)-2,3,4-tri-*O*-mesyl-β-*D*-xylopyranosylamine **4***

From *N*-(2,2-diethoxycarbonylvinyl)-β-D-xylopyranosylamine.[33] x=1.44 mL; y=0.27 mL; z=2.95 mmol; t=24 h; TLC eluant ethyl acetate:ether 3:1; column chromatography (ether:hexane 4:1 and ethyl acetate:hexane 2:1) gave a residue which crystallized from ether (0.176 g, 71%) had m.p. 177–178°C; $[\alpha]_D^{19}$ −33.4 (*c* 0.8); IR ν_{max} 3279, 3028, 2944, 1732, 1663, 1611, 1416, 1356, 1246, 1181, 1071, 1026, 959, and 820 cm^{-1}; ^{1}H NMR: Table 1 and δ 9.34 (dd, 1 H, $J_{NH,=CH}$=12.9, NH), 7.96 (d, 1 H, HC=), 4.94 (t, 1 H, $J_{2,3}$=9.2, H-3), 4.77–4.68 (m, 1 H, H-2), 4.37 (dd, 1 H, $J_{5a,5b}$=12.0, H-5a), 4.26, 4.21 (each q, each 2 H, $^3J_{H,H}$=7.1, 2 CH_2CH$_3$), 3.59 (dd, 1 H, H-5b), 3.26, 3.19, 3.08 (each s, each 3 H, 3 Ms), 1.33, 1.30 (each t, each 3 H, 2 CH$_2$CH_3); ^{13}C NMR: Table 1 and δ 167.8 (C=O chelated), 165.0 (C=O free), 157.0 (HC=), 95.7 (=C), 77.0 (C-3), 73.1 (C-2), 65.0 (C-5), 60.6, 60.3 (each 1 C, 2 CH_2CH$_3$), 39.4 (2C, 2 Ms), 38.4 (Ms), 14.2, 14.0 (each 1 C, 2 CH$_2$CH_3); FABMS *m/z* 576 ([M+Na]$^{+\cdot}$). Anal. Calcd for $C_{16}H_{27}NO_{14}S_3$: C, 34.71; H, 4.92; N, 2.53; S, 17.38. Found: C, 34.68; H, 4.87; N, 2.66; S, 17.29.

General procedure for the preparation of 5–8

To a stirred solution of the corresponding 4-*O*-mesylated *N*-diethoxycarbonylvinyl-D-glycopyranosylamines **1–4** (0.2 mmol) in HMPTA (2 mL) at T°C was gradually added sodium methoxide (0.2 mmol) during t h. The reaction was controlled by TLC until total consumption of the starting material. Compounds **5** and **6** were poured into ice–water (10 mL) and then filtered as white solids. The reaction mixture for **7** and **8** was added into ice–water (10 mL) and extracted with ether (3×10 mL). The organic layer was separated, washed with water (3×10 mL), dried ($MgSO_4$), concentrated to dryness, and the residue purified as indicated.

*1,4-Anhydro-2,3,6-tri-*O*-benzoyl-*N*-(2,2-diethoxycarbonylvinyl)-β-*D*-galactopyranosylamine **5***

T=70°C; t=7.5 h; TLC eluant ether:hexane 2:1; amorphous solid (0.129 g, 100%); $[\alpha]_D^{24}$ +43 (*c* 0.6); IR ν_{max} 2959, 1724, 1601, 1451, 1267, 1113, 1026, and 712 cm^{-1}; ^{1}H NMR: Table 1 and δ 8.08–7.43 (m, 15 H, 3 Ph), 7.76 (s, 1 H, HC=), 5.19–5.18 (m, 1 H, H-2), 5.16 (s, 1 H, H-3), 4.38 (m, 1 H, H-6a), 4.30–4.26 (m, 4 H, H-5, H-6b, CH_2CH$_3$), 4.18 (q, 2 H, $^3J_{H,H}$=7.1, CH_2CH$_3$), 1.25, 1.16 (each t, each 3 H, 2 CH$_2$CH_3); ^{13}C NMR: Table 1 and δ 166.0 (2 C, 2 C=O), 165.7 (2 C, 2 C=O of Bz), 165.6 (C=O of Bz), 145.3 (HC=), 133.6–128.3 (18 C, 3 Ph), 100.3 (C=), 79.7 (C-2), 76.8 (C-3), 74.2 (C-5), 63.4 (C-6), 60.9, 60.6 (each 1 C, 2 CH_2CH$_3$), 14.1, 13.9 (each 1 C, 2 CH$_2$CH_3); FABMS *m/z* 666 ([M+Na]$^{+\cdot}$). Anal. Calcd for $C_{35}H_{33}NO_{11}$: C, 65.31; H, 5.17; N, 2.18. Found: C, 65.25; H, 5.37; N, 2.19.

*1,4-Anhydro-*N*-(2,2-diethoxycarbonylvinyl)-2,3-di-*O*-mesyl-6-*O*-trityl-β-*D*-galactopyranosylamine* **6**

T=70°C; t=12.5 h; TLC eluant ethyl acetate:hexane 1:1; crystallized from ether gave 0.108 g (72%) of a solid which had m.p. 96–98°C; $[\alpha]_D^{27}$ +43 (*c* 1.0); IR ν_{max} 3030, 2949, 1709, 1595, 1356, 1182, 1007, and 864 cm^{-1}; ^1H NMR: Table 1 and δ 7.43–7.25 (m, 15 H, 3 Ph), 7.37 (s, 1 H, HC=), 4.88 (m, 1 H, H-2), 4.69 (d, 1 H, $J_{2,3}$=1.0, H-3), 4.27–4.12 (m, 4 H, 2 CH_2CH_3), 3.81 (dd, 1 H, $J_{5,6b}$=8.1, $J_{5,6a}$=5.6, H-5), 3.29 (dd, 1 H, $J_{6a,6b}$=10.2, H-6a), 3.21, 3.15 (each s, each 3 H, 2 Ms), 2.91 (dd, 1 H, H-6b), 1.29, 1.23 (each t, each 3 H, $^3J_{H,H}$=7.1, 2 CH_2CH_3); ^{13}C NMR: Table 1 and δ 165.7, 165.1 (each 1 C, 2 C=O), 145.5 (HC=), 143.2–127.2 (18 C, 3 Ph), 101.4 (C=), 87.1 (C-Ph_3), 82.5 (C-2), 80.0 (C-3), 74.9 (C-5), 62.2 (C-6), 61.0, 60.5 (each 1 C, 2 CH_2CH_3), 38.5, 38.2 (each 1 C, 2 Ms), 14.1, 13.8 (each 1 C, 2 CH_2CH_3); FABMS *m/z* 752 ($[M+Na]^{+\cdot}$). Anal. Calcd for $C_{35}H_{39}NO_{12}S_2$:C, 57.60; H, 5.39; N, 1.92; S, 8.79. Found: C, 57.49; H, 5.31; N, 1.92; S, 8.71.

*2,3,6-Tri-*O*-acetyl-1,4-anhydro-*N*-(2,2-diethoxycarbonylvinyl)-β-*D*-galactopyranosylamine* **7**

T=30°C; t=10 h; column chromatography (ether:hexane 6:1) of the residue gave an amorphous and hygroscopic solid (0.030 g, 54%) which had $[\alpha]_D^{21}$ +129 (*c* 1.0); IR ν_{max} 2963, 1755, 1588, 1443, 1219, 1028, 868, and 801 cm^{-1}; ^1H NMR: Table 1 and δ 7.62 (s, 1 H, HC=), 4.79 (m, 1 H, H-2), 4.63 (dd, 1 H, $J_{1,3}$=0.8, $J_{2,3}$=1.1, H-3), 4.29–4.15 (m, 4 H, 2 CH_2CH_3), 4.03–3.99 (m, 2 H, H-5, H-6a), 3.96–3.92 (m, 1 H, H-6b), 2.14, 2.12, 2.07 (each s, each 3 H, 3 Ac), 1.31, 1.26 (each t, each 3 H, $^3J_{H,H}$=7.1, 2 CH_2CH_3); ^{13}C NMR: Table 1 and δ 170.5, 170.3, 170.0 (each 1 C, 3 $COCH_3$), 166.1, 165.7 (each 1 C, 2 C=O), 145.5 (HC=), 100.1 (C=), 78.7 (C-2), 76.2 (C-3), 73.7 (C-5), 63.0 (C-6), 60.9, 60.5 (each 1 C, 2 CH_2CH_3), 20.7, 20.6, 20.5 (each 1 C, 3 $COCH_3$), 14.2, 14.0 (each 1 C, 2 CH_2CH_3); FABMS *m/z* 480 ($[M+Na]^{+\cdot}$). HRFABMS *m/z* obsd 458.1664, calcd for $C_{20}H_{27}NO_{11}$+H 458.1662.

*1,4-Anhydro-*N*-(2,2-diethoxycarbonylvinyl)-2,3-di-*O*-mesyl-α-*L*-arabinopyranosylamine* **8**

T=20°C; t=14 h; column chromatography (dichloromethane:nitromethane 3:1) of the residue gave an amorphous and hygroscopic solid (0.058 g, 65%) which had $[\alpha]_D^{24}$ +95 (*c* 0.1); IR ν_{max} 2988, 2942, 1701, 1659, 1611, 1356, 1252, 1177, 1074, 957, 841, and 801 cm^{-1}; ^1H NMR: Table 1 and δ 7.46 (s, 1 H, HC=), 4.88 (m, 1 H, H-2), 4.66 (d, 1 H, $J_{2,3}$=1.2, H-3), 4.34–4.27 (m, 2 H, CH_2CH_3), 4.23 (q, 2 H, $^3J_{H,H}$=7.1, CH_2CH_3), 3.78 (dd, 1 H, $J_{5a,5b}$=8.4, H-5a), 3.69 (d, 1 H, H-5b), 3.18, 3.16 (each s, each 3 H, 2 Ms), 1.34, 1.28 (each t, each 3 H, 2 CH_2CH_3); ^{13}C NMR: Table 1 and δ 165.9, 165.1 (each 1 C, 2 C=O), 144.8 (HC=), 104.8 (C=), 82.3 (C-2), 79.9 (C-3), 64.8 (C-5), 61.4, 60.9 (each 1 C, 2 CH_2CH_3), 38.6, 38.4 (each 1 C, 2 Ms), 14.1, 13.9 (each 1 C, 2 CH_2CH_3); FABMS *m/z* 480 ($[M+Na]^{+\cdot}$); HREIMS *m/z* obsd 457.0695, calcd for $C_{15}H_{23}NO_{11}S_2$ 457.0712.

General procedure for the preparation of ***9–11***

A solution of the corresponding aza-anhydroglycopyranosylamine **5**, **6** and **8** (0.070 mmol) in F_3COOH:H_2O 3:1 (1 mL) was kept at 0°C under nitrogen for t h. The reaction was controlled by TLC until total consumption of the starting material, then was stirred with saturated aqueous sodium hydrogencarbonate (10 mL) for 20 min, and extracted with dichloromethane (3×10 mL). The organic layer was separated, washed with water (3×10 mL), dried ($MgSO_4$), concentrated to dryness, and the residue was purified as indicated.

*2,3,6-Tri-*O*-benzoyl-4-deoxy-4-(2,2-diethoxycarbonylvinyl)amino-*D*-galactopyranose* **9**

(α:β ratio 5:2) t=15 min; column chromatography (dichloromethane:methanol 40:1) of the residue gave an amorphous solid (0.025 g, 55%). IR ν_{max} 2926, 1724, 1659, 1603, 1451, 1265, 1094, 1028, 802, and 710 cm^{-1}; ^1H NMR:[39] Table 1 and δ 9.83–9.78 (m, 1 H, NH′), 9.74 (dd, 1 H, $J_{NH,=CH}$=13.2, NH), 8.04–7.02 (m, 30 H, 6 Ph), 7.88 (d, 2 H, $J_{NH',CH'}$=13.5, CH and CH′), 5.91 (dd, 1 H, $J_{2,3}$=10.8, H-3), 5.57 (dd, 1 H, $J_{2',3'}$=10.3, $J_{3',4'}$=3.8, H-3′), 5.41 (dd, 1 H, $J_{1',2'}$=8.1, H-2′), 5.36 (dd, 1 H, H-2), 4.97 (m, 1 H, H-1′), 4.88 (t, 1 H, $J_{5,6a}$=$J_{5,6b}$=6.0, H-5), 4.64 (dd, 1 H, $J_{6'a,6'b}$=11.4, $J_{5',6'a}$=6.1, H-6′a),

4.58 (dd, 1 H, $J_{6a,6b}$=11.6, H-6a), 4.45 (dd, 1 H, $J_{5',6'b}$=5.8, H-6'b), 4.42 (dd, 1 H, H-6b), 4.32–4.28 (m, 5 H, H-5', 2 CH_2CH_3), 4.10 (dd, 1 H, $J_{4',NH}$=9.7, $J_{3',4'}$=0.0, H-4'), 3.98–3.85 (m, 4 H, 2 CH_2CH_3), 3.37 (bs, 2 H, 2 OH), 1.41–1.37 (m, 6 H, 2 CH_2CH_3), 0.98–0.92 (m, 6 H, 2 CH_2CH_3); ^{13}C NMR: Table 1 and δ 169.0 (2 C, 2 C=O chelated), 165.9, 165.6, 165.5 (each 2 C, 6 C=O of Bz), 164.9 (2 C, 2 C=O), 159.5 (HC'=), 133.8–127.7 (36 C, 6 Ph), 96.6 (C-1'), 94.0 (=C'), 72.2 (C-2'), 71.9 (C-3'), 71.2 (C-5'), 69.3 (C-2), 69.0 (C-3), 65.9 (C-5), 62.7 (C-6), 62.4 (C-6'), 60.2, 59.5, 59.4, 58.6, 55.5 (each 1 C, 4 CH_2CH_3 and C-4'), 14.2, 13.9 (each 2 C, 4 CH_2CH_3); FABMS *m/z* 684 ([M+Na]$^{+\cdot}$). Anal. Calcd for $C_{35}H_{35}NO_{12}$: C, 63.53; H, 5.33; N, 2.12. Found: C, 63.40; H, 5.41; N, 2.25.

*4-Deoxy-4-(2,2-diethoxycarbonylvinyl)amino-2,3-di-*O*-mesyl-*D*-galactopyranose* ***10***

(α:β ratio 1.1:1) t=15 min; column chromatography (ethyl acetate:hexane 3:1) of the residue gave an amorphous solid (0.017 g, 47%). IR ν_{max} 2926, 1724, 1599, 1481, 1443, 1352, 1092, 874, 801, and 746 cm^{-1}; ^{1}H NMR:[39] Table 1 and δ 9.39 (dd, 1 H, $J_{NH,HC'=}$=13.6, NH), 9.29 (dd, 1 H, $J_{NH',HC'=}$=13.6, $J_{NH',4'}$=9.6, NH'), 8.58 (bs, 1 H, OH' anomeric), 8.23 (d, 1 H, $J_{OH,1}$=3.8, OH anomeric), 8.11 (d, 1 H, =CH'), 5.21 (dd, 1 H, $J_{2,3}$=10.3, H-3), 5.09 (bs, 2 H, OH and OH'), 4.86 (m, 1 H, H-1'), 4.83 (dd, 1 H, $J_{2',3'}$=10.0, $J_{3',4'}$=4.2, H-3'), 4.63 (dd, 1 H, H-2), 4.51 (td, 1 H, $J_{5,6a}$=$J_{5,6b}$=6.4, H-5), 4.47 (dd, 1 H, $J_{1',2'}$=7.8, H-2'), 4.29–4.11 (m, 9 H, 4 CH_2CH_3 and H-4'), 3.82 (td, 1 H, $J_{5',6'a}$=$J_{5',6'b}$=6.4, $J_{4',5'}$=0.8, H-5'), 3.75 (dd, 1 H, $J_{6'a,6'b}$=11.0, H-6'a), 3.70 (dd, 1 H, $J_{6a,6b}$=10.6, H-6a), 3.62–3.56 (m, 2 H, H-6b, H-6'b), 3.20, 3.18, 3.14, 3.12 (each s each 3 H, 4 Ms), 1.37–1.26 (m, 12 H, 4 CH_2CH_3); ^{13}C NMR: Table 1 and δ 168.8, 168.6 (each 1 C, 2 C=O chelated), 165.3, 165.0 (each 1 C, 2 C=O free), 160.4 (HC'=), 95.3 (C-1'), 91.8 (=C'), 79.1 (C-2'), 77.6 (C-3'), 75.1 (C-3), 74.8 (C-2), 72.9 (C-5'), 67.1 (C-5), 60.2–59.4 (7 C, C-4', C-6, C-6', 2 CH_2CH_3), 39.0, 38.8, 38.7, 38.5 (each 1 C, 4 Ms), 14.1 (4 C, 2 CH_2CH_3); FABMS *m/z* 528 ([M+Na]$^{+\cdot}$). HRFABMS *m/z* obsd 528.0832, calcd for $C_{16}H_{27}NO_{13}S_2$+Na 528.0822.

*4-Deoxy-4-(2,2-diethoxycarbonylvinyl)amino-2,3-di-*O*-mesyl-*L*-arabinopyranose* ***11***

(α:β ratio 1.1:1) t=10 min; column chromatography (ethyl acetate:hexane 3:1) of the residue gave an amorphous solid (0.018 g, 55%); IR ν_{max} 3372, 2938, 1659, 1609, 1366, 1252, 1177, 1076, 1026, 966, 843,and 804 cm^{-1}; ^{1}H NMR:[39] Table 1 and δ 9.52–9.42 (m, 2 H, NH and NH'), 8.14 (d, 1 H, $J_{NH',CH'-}$=13.7, CH'), 8.12 (d, 1 H, $J_{NH,HC-}$=13.7, HC=), 5.27 (bs, 1 H, OH' or OH), 5.18 (dd, 1 H, $J_{2,3}$=9.7, H-3), 4.87 (dd, 1 H, $J_{2',3'}$=9.6, $J_{3',4'}$=4.1, H-3'), 4.77 (d, 1 H, $J_{1',2'}$=7.5, H-1'), 4.68 (dd, 1 H, H-2), 4.59 (bs, 1 H, OH or OH'), 4.53 (dd, 1 H, $J_{1',2'}$=7.5, H-2'), 4.36 (dd, 1 H, $J_{5a,5b}$=12.6, H-5a), 4.29–4.15 (m, 8 H, 4 CH_2CH_3), 4.10 (dd, 1 H, $J_{5'a,5'b}$=12.8, $J_{4',5'a}$=2.3, H-5'a), 3.98 (ddd, 1 H, $J_{4,NH}$=8.7, H-4'), 3.78 (d, 2 H, H-5b, H-5'b), 3.20, 3.19, 3.16, 3.13 (each s, each 3 H, 4 Ms), 1.37–1.27 (m, 12 H, 4 CH_2CH_3); ^{13}C NMR: Table 2 and δ 169.3, 169.0 (each 1 C, 2 C=O chelated), 165.8, 165.6 (each 1 C, 2 C=O free), 159.6 (2 C, HC= and HC'=), 95.6 (C-1'), 92.1 (=C'), 78.2 (C-2'), 76.4 (C-3'), 73.7 (2 C, C-2, C-3), 64.0 (C-5'), 60.4 (CH_2CH_3), 60.2 (C-5), 60.0 (3 C, 3 CH_2CH_3), 58.4 (2 C, C-4 and C-4'), 39.2 (Ms), 38.8 (2 C, 2 Ms), 38.5 (Ms), 14.2 (4 C, 4 CH_2CH_3); FABMS *m/z* 498 ([M+Na]$^{+\cdot}$). Anal. Calcd for $C_{15}H_{25}NO_{12}S_2$: C, 37.89; H, 5.30; N, 2.95; S, 13.49. Found: C, 38.22; H, 5.25; N, 3.21; S, 12.97.

General procedure for the preparation of ***12–15***

To a solution of the corresponding aza-anhydroglycopyranosylamine **5–8** (0.077 mmol) in acetic anhydride (0.5 mL) at 0°C was added trimethylsilyl trifluoromethanesulfonate (0.01 mL); the solution was kept at r.t. under nitrogen for t h. The reaction was controlled by TLC until total consumption of the starting material, then was stirred with saturated aqueous sodium hydrogencarbonate (8 mL) for 20 min, and extracted with dichloromethane (3×10 mL). The organic layer was separated, washed with water (3×10 mL), dried ($MgSO_4$), concentrated to dryness, and the residue was purified as indicated.

(2R and 2S,3R,4S,5S)-2-Acetoxy-5-[(1'S)-1'-acetoxy-2'-benzoyloxyethyl]-3,4-dibenzoyloxy-1-(2,2-diethoxycarbonylvinyl)pyrrolidine 12

(*2R*:*2S* ratio 1:1); t=3 h; column chromatography (ether:hexane 1:1) of the residue gave an amorphous solid (0.034 g, 60%); IR ν_{max} 2963, 1724, 1599, 1451, 1368, 1260, 1179, 1094, 1026, 802, and 712 cm^{-1}; ^1H NMR:[40] Table 2 and δ 8.17–7.26 (m, 30 H, 6 Ph), 6.05 (t, 1 H, $J_{3,4}$=$J_{4,5}$=2.0, H-4), 5.70–5.67 (m, 3 H, H-3, H-4', H-6), 5.63–5.59 (m, 2 H, H-3', H-6'), 4.93 (dd, 1 H, $J_{7a,7b}$=12.6, $J_{6,7a}$=2.6, H-7a), 4.76 (dd, 1 H, $J_{7a',7b'}$=12.7, $J_{6',7a'}$=1.9, H-7a'), 4.51 (dd, 1 H, $J_{6',7b'}$=5.9, H-7b'), 4.41 (dd, 1 H, $J_{6,7b}$=6.0, H-7b), 4.30–4.10 (m, 8 H, 4 CH_2CH$_3$), 2.13, 2.08, 2.05, 2.02 (each s, each 3 H, 4 COCH$_3$), 1.28, 1.27 (each t, each 6 H, 4 CH$_2$CH_3); ^{13}C NMR: Table 2 and δ 169.6–164.2 (14 C, 14 C=O), 133.7–128.1 (36 C, 6 Ph), 101.6 (=C), 99.9 (=C'), 78.6 (C-4'), 75.6 (C-4), 74.8 (2 C, C-3, C-3'), 71.8 (C-6'), 70.7 (C-6), 63.8 (C-7), 62.9 (C-7'), 60.5 (4 C, 4 *C*H$_2$CH$_3$), 20.6 (1 CO*C*H$_3$), 20.4 (3 C, 3 CO*C*H$_3$), 14.1–13.7 (4 C, 4 CH$_2$*C*H$_3$); FABMS *m/z* 768 ([M+Na]$^{+\cdot}$). HREIMS *m/z* obsd 700.1977, calcd for $C_{37}H_{34}NO_{13}$ 700.2030.

(2R and 2S,3R,4S,5S)-2-Acetoxy-5-[(1'S)-1',2'-diacetoxyethyl]-1-(2,2-diethoxycarbonylvinyl-3,4-dimesyloxy-pyrrolidine 13

(*2R*:*2S* ratio 1:1); t=1 h; column chromatography (ether:hexane 12:1) of the residue gave an amorphous solid (0.036 g, 73%); IR ν_{max} 2963, 1748, 1699, 1611, 1368, 1262, 1179, 1088, 1020, and 970 cm^{-1}; ^1H NMR:[40] Table 2 and δ 5.26 (dd, 1 H, $J_{3,4}$=5.1, $J_{4,5}$=3.2, H-4), 5.22 (ddd, 1 H, $J_{6,7b}$=6.3, $J_{5,6}$=4.8, $J_{6,7a}$=3.3, H-6), 5.17 (dd, 1 H, $J_{6',7'b}$=9.6, $J_{6',7'a}$=4.1, H-6'), 5.14 (s, 1 H, H-4'), 5.10 (t, 1 H, $J_{3,4}$=5.1, H-3), 5.03 (s, 1 H, H-3'), 4.33 (dd, 1 H, $J_{7a,7b}$=12.7, H-7a), 4.29–4.09 (m, 8 H, 4 CH_2CH$_3$), 4.26 (dd, 1 H, $J_{7'a,7'b}$=12.7 H-7'a), 4.25–4.07 (m, 2 H, H-7b, H-7'b), 3.22, 3.12, 3.10, 3.06 (each s, each 3 H, 4 Ms), 2.10–1.99 (m, 18 H, 6 COCH$_3$), 1.27–1.18 (m, 12 H, 4 CH$_2$CH_3); ^{13}C NMR: Table 2 and δ 170.6–165.5 (10 C, 10 C=O), 101.1 (=C'), 98.6 (=C), 78.4 (2 C, C-4, C-4'), 71.4 (2 C, C-3, C-3'), 69.5 (2 C, C-6, C-6'), 62.0–60.9 (6 C, C-7, C-7', 4 *C*H$_2$CH$_3$), 38.9 (2 C, 2 Ms), 38.4, 38.2 (each 1 C, 2 Ms), 20.7, 20.6 (each 3 C, 6 CO*C*H$_3$), 14.1, 13.9 (each 2 C, 4 CH$_2$*C*H$_3$); FABMS *m/z* 654 ([M+Na]$^{+\cdot}$). HRFABMS *m/z* obsd 654.1122, calcd for $C_{22}H_{33}NO_{16}S_2Na$ 654.1138.

(2R and 2S,3R,4S,5S)-2,3,4-Triacetoxy-5-[(1'S)-1',2'-diacetoxyethyl]-1-(2,2-diethoxycarbonylvinyl)-pyrrolidine 14

(*2R*:*2S* ratio 1:3); t=1 h; column chromatography (ethyl acetate:hexane 1:1) of the residue gave an amorphous solid (0.045 g, 69%); IR ν_{max} 2978, 1757, 1694, 1611, 1370, 1227, 1090, 1038, 970, 874, and 801 cm^{-1}; ^1H NMR:[40] Table 2 and δ 5.41 (m, 1 H, H-4), 5.32–5.26 (m, 3 H, H-3, H-6, H-6'), 5.20 (s, 1 H, H-4'), 5.01 (s, 1 H, H-3'), 4.54 (dd, 1 H, $J_{7a,7b}$=12.4 $J_{6,7a}$=3.0, H-7a), 4.38 (dd, 1 H, $J_{7'a,7'b}$=12.3, $J_{6',7'a}$=2.7, H-7'a), 4.32–3.96 (m, 8 H, 4 CH_2CH$_3$), 4.17–4.07 (m, 1 H, H-7'b), 4.10–4.00 (m, 1 H, H-7b), 2.20, 2.15, 2.13, 2.12, 2.08, 2.06 (each s, each 3 H, 6 COCH$_3$), 2.05 (6 H, 2 COCH$_3$), 1.34–1.20 (m, 12 H, 4 CH$_2$CH_3); ^{13}C NMR: Table 2 and δ 169.6–164.7 (7 C, 7 C=O), 100.2 (=C'), 99.2 (=C), 77.3 (C-4'), 75.7 (C-4), 74.5 (C-3'), 73.5 (C-3), 69.3 (2 C, C-6, C-6'), 63.2 (C-7), 61.2 (C-7'), 60.3, 60.1 (each 1 C, 2 *C*H$_2$CH$_3$), 59.7 (2 C, 2 *C*H$_2$CH$_3$), 19.8–19.4 (4 C, 4 CO*C*H$_3$), 13.3 (2 C, 2 CH$_2$*C*H$_3$), 13.1, 13.0 (each 1 C, 2 CH$_2$*C*H$_3$); FABMS *m/z* 582 ([M+Na]$^{+\cdot}$). HREIMS *m/z* obsd 559.1929, calcd for $C_{24}H_{33}NO_{14}$ 559.1901.

(2R and 2S,3R,4S,5S)-2-Acetoxy-5-acetoxymethyl-1-(2,2-diethoxycarbonylvinyl)-3,4-dimesyloxy-pyrrolidine 15

(*R*:*S* ratio 1:3) t=2 h; column chromatography (ethyl acetate:hexane 6:1) of the residue gave an amorphous solid (0.030 g, 69%); IR ν_{max} 2963, 2926, 2853, 1742, 1603, 1366, 1260, 1179, 1094, 1020, and 799 cm^{-1}; ^1H NMR:[40] Table 2 and δ 5.32–5.24 (m, 2 H, H-3, H-4), 5.20 (s, 1 H, H-4'), 5.16 (s, 1 H, H-3'), 4.51–4.15 (m, 4 H, H-6a, H-6b, H-6'a, H-6'b), 4.41–4.15 (m, 8 H, 4 CH_2CH$_3$), 3.31, 3.24, 3.21, 3.18 (each s, each 3 H, 4 Ms), 2.23 (s, 3 H, COCH_3), 2.18 (s, 6 H, 2 COCH_3), 2.16

(s, 3 H, $COCH_3$), 1.43–1.27 (m, 12 H, 4 CH_2CH_3); ^{13}C NMR: Table 2 and δ 170.4 (2 C, 2 $COCH_3$), 170.2, 169.7 (each 1 C, 2 $COCH_3$), 166.1, 165.9, 165.7, 165.5 (each 1 C, 4 C=O), 103.0 (=C'), 102.3 (=C), 80.4 (C-4'), 79.9 (C-4), 77.5 (2 C, C-3, C-3') 61.9–59.9 (6 C, C-6, C-6', 4 CH_2CH_3), 39.1, 38.6 (each 1 C, 2 Ms), 38.5 (2 C, 2 Ms), 20.8, 20.6 (each 2 C, 4 $COCH_3$), 14.2, 14.0 (each 2 C, 4 CH_2CH_3); FABMS *m/z* 582 ($[M+Na]^{+\cdot}$). HRFABMS *m/z* obsd 692.0086, calcd for $C_{19}H_{29}NO_{14}S_2Cs$ 692.0084.

Cleavage of the C1–O bond in the presence of $LiClO_4$

A solution of the corresponding aza-anhydroglycopyranosylamine **5**, **6**, or **8** (0.075 mmol) and lithium perchlorate (0.075 mmol) in methanol (2 mL) at 0°C was stirred for 1 h, and then a 2:1 mixture of trifluoroacetic acid:trifluoroacetic anhydride (0.5 mL) was added, and the solution kept under nitrogen for 0.5 h. The reaction was controlled by TLC until total consumption of the starting material, then the solution was stirred with saturated aqueous sodium hydrogencarbonate (8 mL) for 20 min, and extracted with dichloromethane (3×10 mL); the organic layer was separated, washed with water (3×10 mL), dried ($MgSO_4$) and concentrated to dryness. The reactions on **5**, **6**, and **8** are named as (a), (b), and (c) respectively.

(a) The starting material was **5**. (2*S*,3*R*,4*S*,5*S*)-3,4-Dibenzoyloxy-5-[(1'*S*)-2'-benzoyloxy-1'-hydroxyethyl]-1-(2,2-diethoxycarbonylvinyl)-2-methoxypyrrolidine **16**[36,41] was isolated (0.034 g, 66%) as amorphous solid after preparative TLC (ether:hexane 2:1). Compound **16** had ^1H NMR: Table 2 and δ 8.05–7.26 (m, 15 H, 3 Ph), 5.63 (s, 1 H, H-4), 5.60 (s, 1 H, H-3), 4.85 (dd, 1 H, $J_{7a,7b}$=12.0, $J_{6,7a}$=3.5, H-7a), 4.51 (dd, 1 H, $J_{6,7b}$=6.1, H-7b), 4.37–4.30 (m, 1 H, H-6), 4.37–4.30 (m, 2 H, CH_2CH_3), 4.30 (bs, 1 H, OH), 4.24–4.14 (m, 2 H, CH_2CH_3), 3.45 (s, 3 H, OCH_3), 1.30, 1.26 (each t, each 3 H, $^3J_{H,H}$=7.1, 2 CH_2CH_3); ^{13}C NMR: Table 2 and δ 166.5 (3 C, 3 C=O), 165.5, 164.8 (each 1 C, 2 C=O), 133.7–128.3 (18 C, 3 Ph), 99.2 (=C), 78.0 (C-4), 75.1 (C-3), 70.6 (C-6), 66.5 (C-7), 60.3 (2 C, 2 CH_2CH_3), 54.1 (OCH_3), 14.2, 14.0 (each 1 C, 2 CH_2CH_3); FABMS *m/z* 698 ($[M+Na]^{+\cdot}$). The HRMS was obtained on the acetyl derivative **17**.

(2*S*,3*R*,4*S*,5*S*)-5-[(1'*S*)-1'-Acetoxy-2'-benzoyloxyethyl]-3,4-dibenzoyloxy-1-(2,2-diethoxycarbonylvinyl)-2-methoxypyrrolidine **17**.[36,41] Compound **16** (0.026 mmol) was solved in pyridine:acetic anhydride 1:1 (1 mL), and kept at 0°C for 16 h. The mixture was dryed under diminished pressure; preparative TLC (ether:hexane 2:1) of the residue yield an amorphous solid (0.013 g, 71%); $[\alpha]_D^{28}$ +37 (*c* 0.8); IR ν_{max} 2963, 2918, 1724, 1601, 1451, 1368, 1260, 1094, 1026, 801, and 712 cm^{-1}; ^1H NMR: Table 2 and δ 8.13–7.36 (m, 15 H, 3 Ph), 5.71–5.68 (m, 1 H, H-6), 5.68 (s, 1 H, H-4), 5.60 (s, 1 H, H-3), 5.01 (dd, 1 H, $J_{7a,7b}$=12.4 $J_{6,7a}$=2.1, H-7a), 4.45 (dd, 1 H, $J_{6,7b}$=6.3, H-7b), 4.39–4.11 (m, 4 H, 2 CH_2CH_3), 3.43 (bs, 3 H, OCH_3), 2.05 (s, 3 H, $COCH_3$), 1.32–1.26 (m, 6 H, 2 CH_2CH_3); ^{13}C NMR: Table 2 and δ 166.1–164.9 (6 C, 6 C=O), 133.7–128.3 (18 C, 3 Ph), 99.7 (=C), 77.5 (C-4), 74.9 (C-3), 70.4 (C-6), 63.4 (C-7), 60.5, 60.3 (each 1 C, 2 CH_2CH_3), 53.6 (OCH_3), 20.5 ($COCH_3$), 14.2, 14.0 (each 1 C, 2 CH_2CH_3); FABMS *m/z* 740 ($[M+Na]^{+\cdot}$). HREIMS *m/z* obsd 717.2420, calcd for $C_{38}H_{39}NO_{13}$ 717.2421.

(b) The starting material was **6**. Preparative TLC (dichloromethane:methanol 40:1) of the residue gave (2*RS*,4*S*,6*S*,7*R*,8*S*)-2-diethoxycarbonylmethyl-4-hydroxymethyl-6,7-dimesyloxy-8-methoxy-1-aza-3-oxabicyclo-[3,3,0]-octane **22** (0.033 g, 82.5%) and traces of other two products with FABMS $[M+Na]^{+\cdot}$ 784 and 542 corresponding to (2*S*,3*R*,4*S*,5*S*)-1-(2,2-diethoxycarbonylvinyl)-3,4-dimesyloxy-2-methoxy-5-[(1'*S*)-2'-trityloxy-1'-hydroxyethyl]pyrrolidine **18** and its de-*O*-Tr derivative **19** respectively. Compound **22** had $[\alpha]_D^{28}$ 0 (*c* 0.4); IR ν_{max} 2924, 2855, 1732, 1464, 1368, 1262, 1179, 1094, 964, and 839 cm^{-1}; ^1H NMR: δ 5.48 (d, 1 H, $J_{2,CH}$=9.0, H-2), 5.28 (dd, 1 H, $J_{6,7}$=7.3, $J_{7,8}$=3.2, H-7), 5.16 (dd, 1 H, $J_{5,6}$=3.2, H-6), 4.65 (d, 1 H, H-8), 4.28–4.21 (m, 4 H, 2 CH_2CH_3), 3.98 (m, 1 H, CHH–OH), 3.93–3.89 (m, 2 H, H-4, H-5), 3.75 (m, 1 H, CHH–OH), 3.65 (s, 3 H, OMe), 3.51 [d, 1 H, $CH(CO_2Et)_2$], 3.22, 3.20 (each s, each 3 H, 2 Ms), 1.36–1.23 (m, 6 H, 2 CH_2CH_3); ^{13}C NMR: δ 167.0, 166.3 (each 1 C, 2 C=O), 91.2 (C-8), 88.4 (C-2), 84.0 (C-4), 82.6 (C-7), 80.6 (C-6), 62.4 (C-5), 62.2, 61.7 (each 1 C, 2 CH_2CH_3), 59.9 (CH_2OH), 59.4 (OCH_3), 57.0

[*C*H(CO_2Et)$_2$], 38.3, 38.1 (each 1 C, 2 Ms), 13.7 (2 C, 2 CH_2CH_3). FABMS *m/z* 542 ([M+Na]$^{+\cdot}$). HRFABMS *m/z* obsd 652.0152, calcd for $C_{17}H_{29}NO_{13}S_2$+Cs 652.0135.

(c) The starting material was **8**. Preparative TLC (ethyl acetate:hexane 1:1) of the residue gave (2*S*,3*R*,4*S*,5*S*)-1-(2,2-diethoxycarbonylvinyl)-5-hydroxymethyl-3,4-dimesyloxy-2-methoxypyrrolidine **20** (0.024 g, 47%) and (2*RS*,6*S*,7*R*,8*S*)-2-diethoxycarbonylmethyl-6,7-dimesyloxy-8-methoxy-1-aza-3-oxabicyclo-[3,3,0]-octane **23** (0.026 g, 41%). Compound **20** had ^{1}H NMR: Table 2 and δ 5.40 (s, 1 H, H-3), 5.08 (m, 1 H, H-4), 4.24–4.10 (m, 4 H, 2 C*H*$_2$CH$_3$), 3.80–3.60 (m, 2 H, H-6a, H-6b), 3.49 (s, 3 H, OCH_3), 3.20 (s, 6 H, 2 Ms), 1.35–1.26 (m, 6 H, 2 CH_2CH_3); ^{13}C NMR: Table 2 and δ 166.7, 165.8 (each 1 C, 2 C=O), 96.9 (=C), 80.9 (C-4), 77.8 (C-3), 65.6 (C-6), 62.0, 61.8 (each 1 C, 2 *C*H$_2$CH$_3$), 52.7 (OCH_3), 38.5, 38.4 (each 1 C, 2 Ms), 14.0, 13.8 (each 1 C, 2 CH_2CH_3); FABMS *m/z* 512 ([M+Na]$^{+\cdot}$). The HRMS was obtained on the acetyl derivative **21**. Compound **23** had $[\alpha]_D^{28}$ 0 (*c* 0.5); IR ν_{max} 2924, 2853, 1601, 1443, 1368, 1260, 1092, 1020, and 802 cm^{-1}; ^{1}H NMR: δ 5.41 (d, 1 H, $J_{2,CH}$=8.8, H-2), 5.13 (dd, 1 H, $J_{6,7}$=6.4, $J_{7,8}$=3.6, H-7), 4.88 (t, 1 H, $J_{5,6}$=4.3, H-6), 4.72 (d, 1 H, H-8), 4.23–4.18 (m, 4 H, 2 C*H*$_2$CH$_3$), 4.13 (dd, 1 H, $J_{4a,4b}$=9.4, $J_{4a,5}$=3.1, H4a), 4.09 (dd, 1 H, $J_{4b,5}$=6.3, H4b), 3.90 (m, 1 H, H-5), 3.54 [d, 1 H, C*H*(CO_2Et)$_2$], 3.50 (s, 3 H, OMe), 3.16, 3.15 (each s, each 3 H, 2 Ms), 1.30–1.23 (m, 6 H, 2 CH_2CH_3); ^{13}C NMR: δ 167.7, 165.8 (each 1 C, 2 C=O), 91.2 (C-8), 88.0 (C-2), 83.2 (C-4), 82.2 (C-7), 79.8 (C-6), 63.7 (C-5), 61.9, 60.9 (each 1 C, 2 *C*H$_2$CH$_3$), 57.7 [*C*H(CO_2Et)$_2$], 59.6 (OCH_3), 38.5, 38.3 (each 1 C, 2 OMs), 14.0, 13.8 (each 1 C, 2 CH_2CH_3). FABMS *m/z* 512 ([M+Na]$^{+\cdot}$). HREIMS *m/z* obsd 489.1012, calcd for $C_{16}H_{27}NO_{12}S_2$ 489.0975.

(2S,3R,4S,5S)-5-Acetoxymethyl)-1-(2,2-diethoxy-carbonylvinyl)-3,4-dimesyloxy-2-methoxy-pyrrolidine 21[36,41]

Compound **20** (0.120 mmol) was solved in pyridine:acetic anhydride (1 mL) and kept at 0°C for 24 h. The reaction mixture was evaporated under diminished pressure; preparative TLC (ether:hexane 1:2) of the residue gave an amorphous solid (0.042 g, 65%) which had $[\alpha]_D^{28}$ +27 (*c* 0.9); IR ν_{max} 2984, 2942, 1748, 1697, 1615, 1362, 1086, 966, and 841 cm^{-1}; ^{1}H NMR: Table 2 and δ 5.38 (bs, 1 H, H-3), 5.04 (m, 1 H, H-4), 4.36–4.28 (m, 3 H, H-5, H-6a, H6b), 4.25–4.10 (m, 4 H, 2 C*H*$_2$CH$_3$), 3.45 (s, 3 H, OCH_3), 3.19, 3.18 (each s, each 3 H, 2 Ms), 2.10 (s, 3 H, $COCH_3$), 1.32, 1.29 (each t, each 3 H,, 6 H, 2 CH_2CH_3); ^{13}C NMR: Table 2 and δ 168.1 (*C*OCH_3), 166.7, 166.3 (each 1 C, 2 CO_2Et), 98.6 (=C), 80.9 (C-4), 77.8 (C-3), 65.8 (C-6), 62.0, 61.1 (each 1 C, 2 *C*H$_2$CH$_3$), 55.7 (OCH_3), 39.0 (2 C, 2 Ms), 20.9 (CO*C*H$_3$), 14.3, 14.1 (each 1 C, 2 CH_2CH_3); FABMS *m/z* 554 ([M+Na]$^{+\cdot}$). HRFABMS *m/z* obsd 531.1054, calcd for $C_{18}H_{29}NO_{13}S_2$ 531.1080.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica of Spain for financial support (grant number PB 94/1440 C02-01).

References

1. Greene, T. W.; Wuts, P. G. M. 'Protection of the Amino Group' in *Protective Groups in Organic Synthesis* 2nd ed., Wiley, New York, 1991, Chapter 7, p. 218.
2. Fuentes, J.; Cuevas, T.; Pradera, M. A. *Tetrahedron* **1993**, *49*, 6235–6250 and references therein.
3. Fuentes, J.; Molina, J. L.; Olano, D.; Pradera, M. A. *Tetrahedron: Asymmetry* **1996**, *7*, 203–218, and references therein.
4. For a recent review see García Fernández, J. M.; Ortiz Mellet, C. *Sulfur Rep.* **1996**, *19*, 61–169.
5. Avalos González, M.; Fuentes Mota, J.; Gómez Monterrey, I. M.; Jimenez Requejo, J. L.; Palacios Albarrán, J. C.; Ortiz Mellet, M. C. *Carbohydr. Res.* **1986**, *154*, 49–62.
6. Babiano, R.; Durán, C.; Plumet, J.; Román, E.; Sánchez, E.; Serrano, J. A.; Fuentes, J. *J. Chem. Soc. Perkin Trans I* **1989**, 1923–1926.

7. Ortiz Mellet, C.; Jimenez Blanco, J. L.; García Fernández, J. M.; Fuentes, J. *J. Carbohydr. Chem.* **1995**, *14*, 1133–1152.
8. Pradera, M. A.; Molina, J. L.; Fuentes, J. *Tetrahedron* **1995**, *51*, 923–934.
9. Fuentes, J.; Cuevas, T.; Pradera, M. A. *Tetrahedron* **1993**, *49*, 6235–6250.
10. Fuentes, J., González-Eulate, E.; López-Barba, E.; Robina, I. *J. Carbohydr. Chem.* **1995**, *14*, 79–93.
11. Knapp, S.; Kukkola, P. J.; Sharma, S.; Murali Dhar, T. G.; Naughton, A. B. J. *J. Org. Chem.* **1990**, *55*, 5700–5710 and references therein.
12. For a review see Horton, D.; Wander, J. D. in *The Carbohydrates: Chemistry and Biochemistry* 2nd ed., Pigman, W., Horton, D., Eds, Academic Press, New York, 1980, Vol IB, Chapter 16 pp. 644–760.
13. Karpiesiuk, W.; Banaszek, A.; Zamojsky, A. *Carbohydr. Res.* **1989**, *186*, 156–162.
14. Ponpipom, M. M.; Bugianeri, R.; Walton, E.; Shen, T. Y. *Carbohydr. Res.* **1978**, *65*, 121–131.
15. For syntheses of 1,4-diamino-1,4-dideoxy-D-glucitol derivatives, see Ogawa, T.; Katano, K.; Matsui, M. *Carbohydr. Res.* **1978**, *60*, C-13–C-17.
16. Lehmann, J.; Rob, B.; Wagenknecht, H.-A. A. *Carbohydr. Res.* **1995**, *278*, 176–180. For related compounds see Lehmann, J.; Rob, B. *Tetrahedron: Asymmetry* **1994**, *11*, 2255–2260.
17. Doboshi, K.; Nagaoka, K.; Watanabe, Y.; Nishida, M.; Hasnada, M.; Naganawa, H.; Takita, T.; Takenchi, T.; Umezawa, H. *J. Antibiotic.* **1985**, *38*, 1166–1170.
18. Vogel, C.; Gries, P. *J. Carbohydr. Chem.* **1994**, *13*, 37–46.
19. (a) Halcomb, R. L.; Wittman, M. D.; Olson, S. H.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 5080–5082. (b) Hoeksema, H.; Bannister, B.; Birkenmeyer, R. D.; Kagan, F.; Magerlein, B. J.; Mackellar, F. A.; Schroeder, W.; Slomp, G.; Herr, R. R. *J. Am. Chem. Soc.* **1964**, *86*, 4223–4224. (c) Hoeksema, H. *J. Am. Chem. Soc.* **1964**, *86*, 4224–4225.
20. Buchanan, J. G.; Jigajinni, V. B.; Singh, G.; Wightmann, R. H. *J. Chem. Soc. Perkin Trans. I* **1987**, 2377–2384.
21. Trucsheit, E.; Frommer, W.; Junge, B.; Müller, L.; Schmidt, D. D.; Wingender, W. *Angew. Chem. Int. Ed.* **1981**, *20*, 744–761.
22. (a) Lay, L.; Nicotra, F.; Paganim, A.; Pangrazio, C.; Panza, L., *Tetrahedron Lett.* **1993**, *22*, 4555–4558. (b) Gruters, R. A.; Neefjes, J. J.; Tersmette, M.; de Goede, R. E. Y.; Tulp, A.; Huisman, H.-G.; Miedema, F.; Ploegls, H. L. *Nature* **1987**, *330*, 74–77.
23. Liu, P. S.; Hoekstra, W. J.; King, C.-H. R. *Tetrahedron Lett.* **1990**, *31*, 2829–2832 and references therein.
24. Buchanan, J. G.; Edgar, A. R.; Hewitt, B. D. *J. Chem. Soc. Perkin Trans. I* **1987**, 2371–2375.
25. Chorgade, M. S.; Ceseke, C. T.; Liu, P. S. *Tetrahedron: Asymmetry* **1994**, *5*, 2251–2254.
26. Hiranuma, S.; Kajimoto, T.; Kanie, O.; Wong, C. H. Presented at the XVIII International Carbohydrate Symposium, Milan, Italy, July 21–26, 1996, Abstract BP116, p. 371.
27. Tatsuta, K.; Kitagawa, M. *Tetrahedron Lett.* **1995**, *36*, 6717–6721. See also Tatsuta, K. Presented at the Second Euroconference on Carbohydrate Mimics, Lago di Garda, Italy, July 16–19, 1996, Abstract IL2.
28. Cipolla, L.; Lay, L.; Nicotra, F.; Pangrazio, C.; Panza, L. *Tetrahedron* **1995**, 51, 4679–4690 and references therein. See also Lay *et al.*[22a]
29. Yuan, J.; Martin, O. R. Presented at the XVIII International Carbohydrate Symposium, Milan, Italy, July 21–26, 1996, Abstract BO034, p. 235.
30. Pradera, M. A.; Olano, D.; Fuentes, J. *Tetrahedron Lett.* **1995**, *36*, 8653–8656.
31. Fuentes Mota, J.; García Fernández, J. M.; Ortiz Mellet, C.; Pradera Adrián, M. A.; Babiano Caballero, R. *Carbohydr. Res.* **1989**, *188*, 35–44.
32. Fuentes Mota, J.; Fernández-Bolaños Guzmán, J.; García Fernández, J. M.; Moreda, W.; Ortiz, C.; Pradera, M. A.; Robina, I.; Welsh, C. *Carbohydr. Res.* **1992**, *232*, 47–57.
33. Gómez Sánchez, A.; Gómez Guillén, M.; Cert Ventulá, A.; Scheidegger, U. *An. Quim.* **1968**, *64B*, 579–590.

34. Lowary, T. L.; Bundle, D. R. *Tetrahedron: Asymmetry* **1994**, *5*, 2397–2404.
35. Zottola, M.; Venkasteswara Rao, B.; Fraser Reid, B. *J. Chem. Soc. Chem. Commun.* **1991**, 969–970.
36. In compounds **16**, **17**, **20**, and **21** the alphabetic order of the substituents would change the numbering of the pyrrolidine ring with respect to **12–15**, being the C-5 that carrying the methoxy group. Nevertheless, for clarity in the discussion we have used the same numbering in all the pyrrolidine compounds **12–21**.
37. Bundle, D. R.; Lemieux, R. U. *Methods Carbohydr. Chem.* **1976**, *VII*, 79–86.
38. Molyneux, R. J.; Benson, M.; Wong, R. Y.; Tropea, J. E.; Elbein, A. D. *J. Nat. Prod.* **1988**, *51*, 1198–1206.
39. The β-anomer is named as ′.
40. The signals indicated as ′ correspond to the *2S* isomer.
41. The correct IUPAC numbering for **16** and **17** as examples are (*2S,3S,4R,5S*)-3,4-dibenzoyloxy-2[(1′S)-2′-benzoyloxy-1′-hydroxyethyl]-1-(2,2-diethoxycarbonylvinyl)-5-methoxypyrrolidine **16** and (*2S,3S,4R,5S*)-2[(1′S)-1′-acetoxy-2′-benzoyloxyethyl]-3,4-dibenzoyloxy-1-(2,2-diethoxycarbonyl-vinyl)-5-methoxypyrrolidine **17**.

(*Received in UK 22 August 1997*)