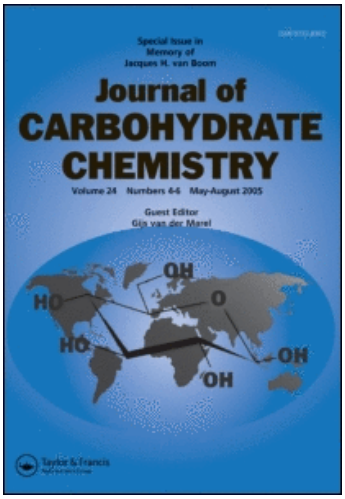

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PREPARATION AND REACTIVITY OF SOME 3-DEOXY-D-ALTRONIC ACID DERIVATIVES

María de Gracia García-Martín[a]; María Violante de Paz Báñez[b]; Juan A. Galbis[a]
[a] Departamento de Química Orgánica y Farmacéutica, Facultad de Farmacia, Universidad de Sevilla, Sevilla, Spain [b] Departamento de Ingeniería Química, Química Física y Química Orgánica, Universidad de Huelva, Huelva, Spain

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PREPARATION AND REACTIVITY OF SOME 3-DEOXY-D-ALTRONIC ACID DERIVATIVES

María de Gracia García-Martín[1], María Violante de Paz Báñez,[2] and Juan A. Galbis[1,*]

[1]Departamento de Química Orgánica y Farmacéutica,
Facultad de Farmacia, Universidad de Sevilla, 41012 Sevilla, Spain
[2]Departamento de Ingeniería Química,
Química Física y Química Orgánica, Universidad de Huelva,
21071 Huelva, Spain

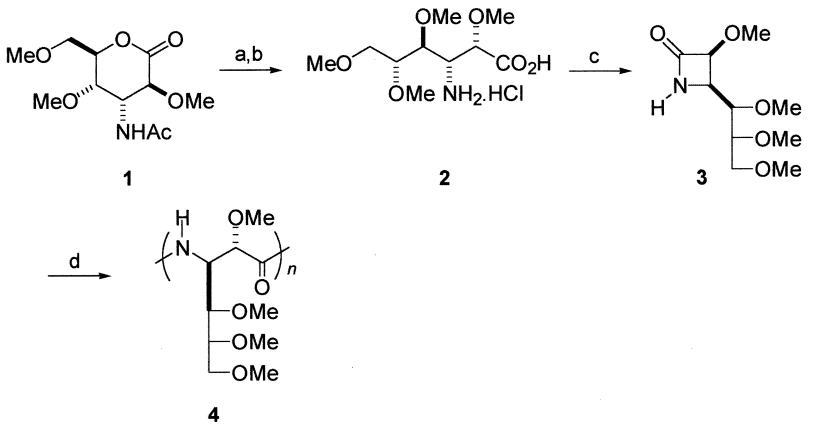
ABSTRACT

3-Amino-3-deoxy-2,4,5,6-tetra-*O*-methyl-D-altronic acid hydrochloride was the key intermediate in the preparation of poly[(2*S*,3*R*)-2-methoxy-3-(D-*erythro*-trimethoxypropyl)propanamide], a chiral nylon 3 analog. We now describe an alternative synthetic route to this amino acid and the unexpected reactivity of some of its 3-deoxy derivatives. Attempts to open the 3-azido-3-deoxy-tri-*O*-methyl (or *O*-benzyl)-D-altrono-1,5-lactone intermediates gave mixtures of products, mostly, α,β-unsaturated carbonyl compounds.

INTRODUCTION

Poly(β-peptide)s, which can be envisaged as nylon 3 derivatives, are able to adopt regular folded structures stabilized by intramolecular hydrogen bonds with features very similar to the α-helix characteristic of poly(α-peptide)s. Recently, it has been demonstrated[1–3] that not only main chain substitution but also the constitution and position of the substituents are determinant for the conformation adopted by poly(β-peptide)s and more specifically for the type of helix that they may form. On the other hand, synthetic polymers containing carbohydrate units in

*Corresponding author.



1 2 3 4

(a) MeI, KOH, THF; (b) 4M HCl; (c) 1. EDPA, MeCN; 2. MsCl, $NaHCO_3$, MeCN; (d) KO^{t}Bu, CH_2Cl_2.

Scheme 1.

the main chain are considered as a new type of polymeric material[4] due to their potential as biodegradable and biocompatible materials useful for medical applications.

We have recently described the preparation of 3-amino-3-deoxy-2,4,5,6-tetra-*O*-methyl-D-altronic acid hydrochloride (**2**) through the 3-acetamido-3-deoxy-2,4,6-tri-*O*-methyl-D-altrono-1,5-lactone (**1**)[5]. This aminoaldonic acid was transformed into the corresponding β-lactam, (3*S*,4*R*)-3-methoxy-4-(D-*erythro*-trimethoxypropyl)azetidine-2-one (**3**), which was further polymerized by anionic ring-opening polymerization to give poly[(2*S*,3*R*)-2-methoxy-3-(D-*erythro*-trimethoxypropyl)propanamide] (4), a chiral nylon 3 analog (Scheme 1)[5]. Due to increasing interest in enantiomerically pure β-amino acids, we tried some alternative approaches to the preparation of *O*-benzyl and *O*-methyl derivatives of the 3-amino-3-deoxy-D-altronic acid. Thus, we attempted to prepare the aminoaldonic acid **2** by opening the lactone ring of 3-azido-3-deoxy-2,4,6-tri-*O*-methyl-D-altrono-1,5-lactone (**13**) which is a precursor of **1**, but complex mixtures of products, mainly α,β-unsaturated carbonyl compounds, were formed. Likewise, the 3-azido-3-deoxy-2,4,6-tri-*O*-benzyl-D-altrono-1,5-lactone (**10**) behaved in a similar way. We now describe an alternative synthetic route to the amino acid **2**, the preparation of lactones **10** and **13** and some other derivatives, and some results on their chemical reactivity.

RESULTS AND DISCUSSION

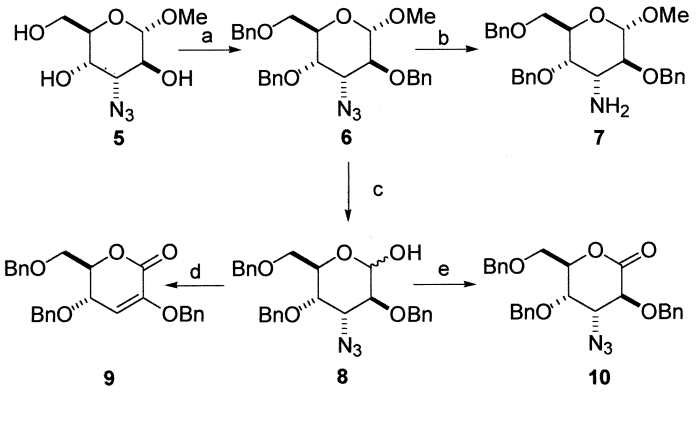
Per-*O*-benzylation of **5** to obtain **6** (Scheme 2) was carried out with benzyl bromide in the presence of sodium hydride in DMF (92%). The *O*-methyl group of **6** was hydrolyzed with 4M hydrochloric acid in acetonitrile at 85°C, and the tri-*O*-

benzyl derivative **8** was obtained in a 75% yield. Oxidation of **8** with pyridinium chlorochromate (PCC) in dichloromethane afforded a good yield (56%) of the corresponding 3-azido-3-deoxy-tri-*O*-benzyl-1,5-D-altrono-lactone (**10**). However, attempts to oxidize **8** with dimethyl sulfoxide-acetic anhydride (1:1) gave rise to a complex mixture of products, from which 6% of the α,β-unsaturated lactone **9** could be isolated. The latter compound could have been formed by β-elimination of the azido group from the preformed lactone **10**.

In a similar way, PCC oxidation of **12** gave the lactone **13** (Scheme 3). Opening of lactones **10** and **13** with methyl iodide as described previously [5–7] was unsuccessful. Under those conditions very complex mixture of products were formed, most of them showing (TLC) intense absorbance under UV light which, together with the NMR data, indicated the presence of conjugated unsaturated systems.

We could verify that these compounds, having a β-azido carbonyl system, suffered β-elimination of the azido group under basic conditions, even with bases as weak as triethylamine. The driving force for this process could be the high stability of the α,β-unsaturated carbonyl system and the favorable entropic factor. The β-elimination of benzoate and benzyl groups from 1,5-aldonolactones[8, 9] and 1,5-aldonolactams[10] respectively, had been reported to give the corresponding α,β-unsaturated derivatives. Earlier studies from our laboratory also described[11] the β-elimination of the methoxy group at *C*-3 of 2,3,4-tri-*O*-methyl-D-xylono (and L-arabinono)-1,5-lactones.

We also undertook the opening of lactone **13** under acidic conditions (Scheme 3). Its reaction with camphorsulfonic acid in dry methanol at room temperature for 7 h, afforded **14** in 94% yield, whereas reaction of **13** with methyl orthoformate in methanol, in the presence of sulfuric acid at 50°C, afforded only a 35% yield of **14**. When trifluoromethanesulfonic acid was used instead of sulfuric acid, **14** was isolated in 59% yield.



(a) NaH, BnBr, DMF; (b) H_2, 10% Pd-C, MeOH; (c) 3:5 4M HCl-MeCN; (d) DMSO, Ac_2O; (e) PCC, CH_2Cl_2.

Scheme 2.

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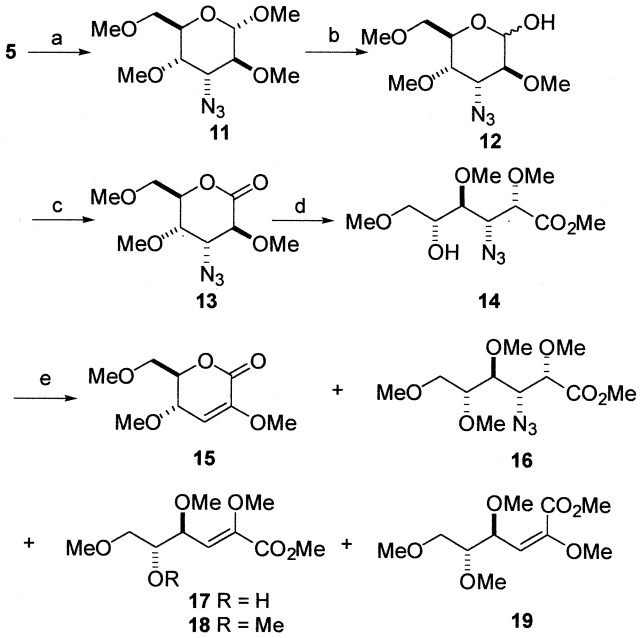
We tried the methylation of OH-5 of **14** by several different methods. Compound **14** was recovered unaltered after treatment with diazomethane in diethyl ether in the presence of silica gel for 6 days, whereas when **14** was treated with sodium hydride/methyl iodide in dry DMF, β-elimination reactions took place, and unsaturated compounds **15** and **17**–**19** were isolated in 20%, 18%, 33% and 28% yields, respectively. However, treatment of **14** with methyl iodide and silver oxide under different conditions gave the desired product **16** in moderate to low yields. Most of these experiments produced **16** along with lactone **13**, α,β-unsaturated lactone **15** and, in some cases, other unsaturated compounds. The reduction of the azido group at C-3 of **16** took place easily with hydrogen and 10% Pd/C, and the intermediate methyl 3-amino-3-deoxy-2,4,5,6-tetra-*O*-methyl-D-altronate was hydrolyzed with 4M hydrochloric acid to give 3-amino-3-deoxy-2,4,5,6-tetra-*O*-methyl-D-altronic acid hydrochloride (**2**).

In order to prevent elimination reactions, the azido groups of **6** and **11** were reduced with hydrogen in the presence of 10% Pd/C in methanol, and the amino compounds **7** and **20** were obtained in good yields. Hydrolysis of the methyl glycoside **20** (Scheme 4) with 4M hydrochloric acid-acetonitrile gave **21** in 85% yield, and the amino group was protected as *N*-benzyloxycarbonyl derivative to give **22**. Oxidation of **22** with PCC in dichloromethane yielded lactone **23** (87%). However, treatment of **23** with methyl iodide, under the conditions known[5–7] to open the



a) MeI, KOH, DMSO; (b) 5:1 4M HCl-MeCN; (c) PCC, CH_2Cl_2; (d) camphorsulfonic acid, MeOH; (e) MeI, NaH or Ag_2O (different conditions gave variable ratio of products).

Scheme 3.

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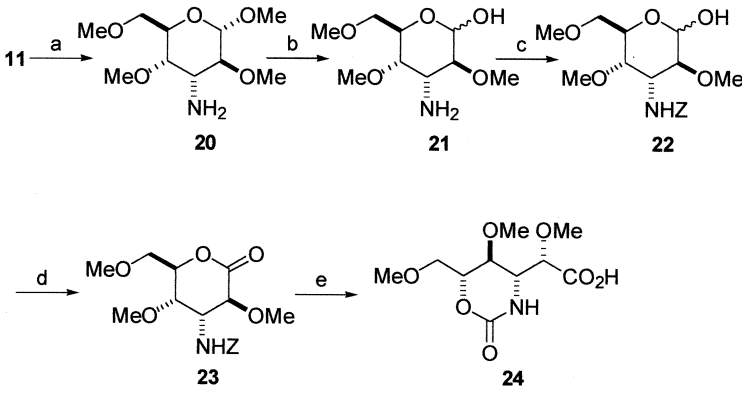

(a) H_2, 10% Pd-C, MeOH; (b) 5:1 4M HCl-MeCN; (c) aq $NaHCO_3$, ZCl; (d) PCC, CH_2Cl_2; (d) MeI, KOH, THF; Z = $COOCH_2Ph$.

Scheme 4.

lactone ring with methylation of OH-5, gave the cyclic urethane **24** (60%). The formation of **24** could be explained as nucleophilic attack by the free OH-5, of the corresponding open chain derivative, on the carbonyl of the *N*-protecting group, with displacement of the benzyloxy group.

In conclusion, due to the easy elimination of the azido group at C-3 of lactone **13**, attempts to open the lactone ring under basic conditions did not give good yields of **16**, the precursor of the amino acid **2**, but mixtures of α,β-unsaturated carbonyl compounds were obtained instead. However, compound **16** was obtained in low to moderate yield, in two steps, by treatment of **13** with camphorsulfonic acid, then methylation of OH-5 of **14**, under mild conditions, with silver oxide and methyl iodide. Alternatively, as we have already described[5] the amino acid **2** was prepared from the acetamido lactone **1**. Lactones **13** and **1** were both easily obtained from **12**.

EXPERIMENTAL

General Methods. Chemicals were all used as purchased from the Aldrich Chemical Co. Solvents were dried and purified, when necessary, by appropriate standard procedures. Melting points are uncorrected. Optical rotations were measured at 20 ± 5°C with a Bellingham & Standley Inc., P20 polarimeter (5-cm cell). TLC was performed on Silica Gel 60 F_{254} (Merck) with detection by UV light or charring with sulfuric acid and flash column chromatography with Silica Gel 60 (230–400 mesh, Merck). Elemental analyses were determined in the Microanalysis Laboratories at the Universidad Complutense de Madrid. FT IR spectra: films or KBr discs. NMR spectra: chemical shifts are reported as parts per million down field from tetramethylsilane. MS were recorded on a Kratos MS80RFA instrument

equipped with a combined EI-CI source. HRMS (EI. 70 eV) were taken with 10000.

3-Amino-3-deoxy-2,4,5,6-tetra-*O*-methyl-D-altronic acid hydrochloride (2). A solution of **16** (0.025 g, 0.086 mmol) in methanol (1 mL) was stirred with 10% Pd/C (3 mg) for 2 h under a hydrogen atmosphere. The suspension was filtered through diatomaceous earth and the solution concentrated to dryness. The residue was purified by flash-column chromatography (ethyl acetate) to give a compound (0.022 g, 97%) that was identified as methyl 3-amino-3-deoxy-2,4,5,6-tetra-*O*-methyl-D-altronate, according to the following data: IR 3420, 1630 (NH_2), 1750 cm^{-1} (CO ester); ^{13}C NMR ($CDCl_3$, 50 MHz), δ 170.74 (C-1), 81.24, 78.23, 77.64 (C-2/C-4/C-5), 69.82 (C-6), 59.80, 59.16, 58.60, 57.65 (4 OCH_3), 54.32 (C-3), 52.45 ($COO\underline{C}H_3$). The above compound was treated with 4M HCl (2 mL) at room temperature for 5 days, then concentrated. The residue was treated with light petroleum to give a solid which was identified as the previously described **2**[5] (0.024 g, 93%).

Methyl 3-azido-3-deoxy-2,4,6-tri-*O*-benzyl-α-D-*altro*-hexopyranoside (6). To sodium hydride (60%) (0.12 g, 3.05 mmol) washed with pentane (20 mL × 3) under argon atmosphere, a solution of **5**[5] (0.13 g, 0.61 mmol) in dry DMF (7 mL) was added dropwise with stirring at 0°C. The mixture was stirred at this temperature for 1 h, then benzyl bromide (0.24 mL, 2.05 mmol) was added and stirring was continued at room temperature overnight. Methanol (2.5 mL) was added dropwise and the mixture was stirred for 1 h, then the reaction mixture was poured into a mixture of $CHCl_3$ (50 mL) and aq $NaHCO_3$ satd solution (25 mL). The organic phase was washed with brine (25 mL), dried (anhydrous $MgSO_4$) and concentrated. The yellowish residue was purified by flash-column chromatography (1:2 diethyl ether-light petroleum) to give the title compound as an oil (0.28 g, 92%); $[\alpha]_D$ +52° (*c* 1.3, dichloromethane); IR 3030 (Ph), 2100 (N_3), 747, 701 cm^{-1} (Ph); ^1H NMR ($CDCl_3$, 200 MHz), δ 7.35–7.25 (m, 15 H, 3 Ph), 4.69 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1), 4.68–4.46 (6 H, 3 $OC\underline{H}_2Ph$), 4.12–3.96 (m, 3 H, H-4, H-6, H-6′), 3.83 (ddd, 1 H, $J_{2,3}$ 4.7, $J_{3,4}$ 3.4, $J_{1,3}$ 0.6 Hz, H-3), 3.68 (m, 1 H, H-5), 3.63 (dd, 1 H, H-2), 3.38 (s, 3 H, OCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz), δ 137.99, 137.48, 137.31, 128.33, 128.28, 128.19, 128.08, 127.82, 127.64 (Ph), 99.89 (C-1), 77.64 (C-2), 73.35 ($O\underline{C}H_2Ph$), 72.65 (C-4), 72.43, 72.24 (2 $O\underline{C}H_2Ph$), 69.06 (C-6), 67.91 (C-5), 59.08 (C-3), 55.34 (OCH_3); MS (CI): *m/z* 462 $(M + H - N_2)^+$, 430 $(M - N_2 - OCH_3)^+$, 91 $(Ph\text{-}CH_2)^+$.

Anal. Calcd for $C_{28}H_{31}N_3O_5$: C, 68.69; H, 6.38; N, 8.58. Found: C, 68.39; H, 6.28; N, 8.35.

Methyl 3-amino-3-deoxy-2,4,6-tri-*O*-benzyl-α-D-*altro*-hexopyranoside (7). A solution of **6** (0.45 g, 0.93 mmol) in methanol (3 mL) was stirred with 10% Pd/C for 4–5 h at room temperature under a hydrogen atmosphere, at atmospheric pressure. The mixture was diluted with methanol, filtered on diatomaceous earth and concentrated. Purification of the residue by flash-column chromatography (ethyl acetate) afforded the corresponding amino derivative **7** (0.42 g, 98%) as an

oil; $[\alpha]_D$ +58° (*c* 1.86, dichloromethane); IR 3382, 1606 (NH_2), 746, 701 cm^{-1} (Ph); ^1H NMR ($CDCl_3$, 500 MHz), δ 7.40–7.20 (m, 15 H, 3 Ph), 4.72 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 4.62 (d, 1H, *J* 12.1 Hz, OC$\underline{H}_2$Ph), 4.60 (d, 1H, *J* 12.1 Hz, OC$\underline{H}_2$Ph), 4.58 (d, 1H, *J* 12.1 Hz, OC$\underline{H}_2$Ph), 4.56 (d, 1H, *J* 12.1 Hz, OC$\underline{H}_2$Ph), 4.52 (d, 1H, *J* 11.4 Hz, OC$\underline{H}_2$Ph), 4.43 (d, 1H, *J* 11.4 Hz, OC$\underline{H}_2$Ph), 3.97 (ddd, 1 H, $J_{4,5}$ 9.5, $J_{5,6}$ 2.4, $J_{5,6'}$ 5.3 Hz, H-5), 3.82 (dd, 1 H, $J_{3,4}$ 3.8 Hz, H-4), 3.77 (dd, 1 H, $J_{6,6'}$ 10.7 Hz, H-6), 3.73 (dd, 1 H, H-6′), 3.62 (dd, 1 H, $J_{2,3}$ 3.8 Hz, H-2), 3.39 (s, 3 H, OCH_3), 3.37 (t, 1 H, H-3); ^{13}C NMR ($CDCl_3$, 125 MHz), δ 138.33, 138.05, 137.93, 128.37, 128.26, 127.84, 127.77, 127.67 (Ph), 100.26 (C-1), 77.63 (C-2), 73.45 (O$\underline{C}H_2$Ph), 73.08 (C-4), 72.06 (O$\underline{C}H_2$Ph), 71.43 (O$\underline{C}H_2$Ph), 69.79 (C-6), 66.69 (C-5), 55.21 (OCH_3), 49.30 (C-3); MS (CI): *m/z* 464 $(M + H)^+$, 432 $(M - OCH_3)^+$, 91 $(Ph\text{-}CH_2)^+$.

Anal. Calcd for $C_{28}H_{33}NO_5$: C, 72.55; H, 7.18; N, 3.02. Found: C, 72.53; H, 7.11; N, 2.74.

3-Azido-3-deoxy-2,4,6-tri-*O*-benzyl-α,β-D-*altro*-hexopyranose (8). A solution of **6** (2.17 g, 4.44 mmol) in a 3:5 mixture of 4M HCl-acetonitrile (80 mL) was heated at 85°C for 4 days. The organic layer was washed with aq $NaHCO_3$ satd solution (15 mL × 3) and the aqueous solution extracted with Cl_3CH (75 mL × 3). The combined organic solutions were dried (anhydrous $MgSO_4$) and concentrated to dryness. The residue was purified by flash-column chromatography (2:1 diethyl ether-light petroleum) giving a small amount of the starting material **6** (0.18 g, 8%), and **8** as an oil (1.45 g, 75%); $[\alpha]_D$ +14° (*c* 1.4, dichloromethane); IR 3425 (OH), 3030 (Ph), 2110 (N_3), 742, 699 cm^{-1} (Ph); ^{13}C NMR ($CDCl_3$, 50 MHz), δ 137.99–137.28, 128.67–127.61 (Ph) 92.94, 91.20 (C-1α/C-1β), 78.15, 77.63 (C-2α/C-2β), 73.54, 73.19, 72.45, 72.14 (O$\underline{C}H_2$Ph), 74.29, 72.78, 72.65, 67.58 (C-4α,β/C-5α,β), 68.96 (C-6α and C-6β), 59.79, 59.33 (C-3α/C-3β); MS (CI): *m/z* 340 $(M - OCH_2Ph - N_2)^+$, 91 $(Ph\text{-}CH_2)^+$.

Anal. Calcd for $C_{27}H_{29}N_3O_5$: C, 68.19; H, 6.15; N, 8.84. Found: C, 67.82; H, 6.26; N, 8.68.

3-Deoxy-2,4,6-tri-*O*-benzyl-D-*erythro*-hex-2-enono-1,5-lactone (9). A solution of **8** (0.12 g, 0.25 mmol) in 1:1 dry Me_2SO-acetic anhydride (4 mL) was stirred at room temperature under an argon atmosphere for 2 days. The mixture was poured into iced H_2O (15 mL) containing Et_3N (1 mL) and extracted with diethyl ether (20 mL × 3). The organic solution was dried (anhydrous $MgSO_4$) and concentrated to dryness. TLC of the residue showed a complex mixture of products and flash-column chromatography (1:5 ethyl acetate-light petroleum, containing 1% of Et_3N) afforded the title compound as an oil (0.007 g, 6%); IR 3030 (Ph), 1744 (CO lactone), 1640 (C=C), 736, 690 cm^{-1} (Ph); ^1H NMR ($CDCl_3$, 500 MHz), δ 7.34–7.24 (m, 15 H, Ph), 5.63 (d, 1 H, $J_{3,4}$ 4.1 Hz, H-3), 4.89, 4.86 (2d, each 1 H, *J* 12.1 Hz, C$\underline{H}_2$Ph), 4.58–4.46 (m, 6 H, H-4, H-5, 2C$\underline{H}_2$Ph), 3.73 (dd, 1 H, $J_{5,6}$ 3.9, $J_{6,6'}$ 10.7 Hz, H-6), 3.65 (dd, 1 H, $J_{5,6'}$ 4.7 Hz, H-6′); ^{13}C NMR ($CDCl_3$, 125 MHz), δ 159.37 (C-1), 144.02 (C-2),137.41–127.34 (Ph), 110.16 (C-3), 79.74/69.34 (C-4/C-5), 73.54 (C-6), 71.11, 70.33, 68.28 (3 O$\underline{C}H_2$Ph); MS (CI): *m/z* 339 $(M - C_7H_7)^+$, 181 $(C_7H_7\ C_7H_6)^+$, 91 $(C_7H_7)^+$.

3-Azido-3-deoxy-2,4,6-tri-*O*-benzyl-D-altrono-1,5-lactone (10). A solution of **8** (0.16 g, 0.34 mmol) in dry CH_2Cl_2 (12 mL) was stirred with 3Å molecular sieves (0.15 g) for a few minutes, then pyridinium chlorochromate (0.36 g, 1.68 mmol) was added. The mixture was stirred at room temperature in the dark for 2 days, then diluted with diethyl ether, filtered through a column of silica gel G containing $CaSO_4$ (10%), and concentrated to give **10** as a colorless oil (0.1 g, 56%); $[\alpha]_D$ −44° (*c* 0.68, dichloromethane); IR 3031 (Ph), 2110 (N_3), 1748 (C=O lactone), 742, 699 cm^{-1} (Ph); ^1H NMR ($CDCl_3$, 500 MHz), δ 7.60–7.25 (m, 15 H, 3 Ph), 5.12 (d, 1 H, *J* 11 Hz, OC$\underline{H}_2$Ph), 4.74 (d, 1 H, *J* 11 Hz, OC$\underline{H}_2$Ph), 4.72 (d, 1 H, *J* 11.6 Hz, OC$\underline{H}_2$Ph), 4.66 (d, 1 H, *J* 11.6 Hz, OC$\underline{H}_2$Ph), 4.60 (d, 1 H, *J* 12 Hz, OC$\underline{H}_2$Ph), 4.58 (m, 1 H, H-5), 4.52 (d, 1 H, *J* 12 Hz, OC$\underline{H}_2$Ph), 4.36 (d, 1 H, $J_{2,3}$ 8.7 Hz, H-2), 4.20 (dd, 1 H, $J_{3,4}$ 3.2 Hz, H-3), 4.15 (dd, 1 H, $J_{4,5}$ 4.1 Hz, H-4), 3.69 (dd, 1 H, $J_{5,6}$ 4.1, $J_{6,6'}$ 10.9 Hz, H-6), 3.65 (dd, 1 H, $J_{5,6'}$ 3.1 Hz, H-6′); ^{13}C NMR ($CDCl_3$, 125 MHz), δ 168.37 (C-1), 136.69, 128.44, 128.31, 128.11, 127.95, 127.83, 127.59 (Ph), 78.15 (C-5), 74.46 (C-2), 73.86 (C-4 and O$\underline{C}H_2$Ph), 73.54, 72.90 (2 O$\underline{C}H_2$Ph), 68.66 (C-6), 60.01 (C-3); MS (CI): *m/z* 181 $(C_7H_7C_7H_6)^+$, 91 $(Ph\text{-}CH_2)^+$.

Anal. Calcd for $C_{27}H_{27}N_3O_5$: C, 68.49; H, 5.75; N, 8.87. Found: C, 68.27; H, 5.76; N, 8.61.

3-Azido-3-deoxy-2,4,6-tri-*O*-methyl-D-altrono-1,5-lactone (13). Compound **13** was prepared from **12**[5] (1.2 g, 4.86 mmol) by the same procedure described for **10**, and obtained as a colorless oil (1.1 g, 92%); $[\alpha]_D$ −29° (*c* 1.17, dichloromethane); IR 2112 (N_3), 1752 cm^{-1} (CO lactone); ^1H NMR ($CDCl_3$, 200 MHz), δ 4.51 (q, 1 H, $J_{5,6} = J_{5,6'}$ 3.5 Hz, H-5), 4.15 (dd, 1 H, $J_{3,4}$ 3.0 Hz, H-3), 4.03 (d, 1 H, $J_{2,3}$ 9.2 Hz, H-2), 3.75 (t, 1 H, $J_{4,5}$ 3.3 Hz, H-4), 3.58 (d, 2 H, H-6, H-6′), 3.66, 3.49, 3.36 (s, each 3 H, OCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz), δ 168.59 (C-1), 77.47 (C-5), 77.00 (C-4), 76.92 (C-2), 71.76 (C-6), 59.71 (C-3), 60.21, 59.72, 58.45 (3 OCH_3); MS (CI): *m/z* 246 $(M + H)^+$.

Anal. Calcd for $C_9H_{15}N_3O_5$: C, 44.08; H, 6.16; N, 17.14. Found: C, 44.11; H, 6.04; N, 17.07.

Methyl 3-azido-3-deoxy-2,4,6-tri-*O*-methyl-D-altronate (14). A solution of lactone **13** (0.16 g, 0.65 mmol) in dry MeOH (10 mL) containing camphorsulfonic acid (6 mg) was stirred at room temperature for 6 h. The solution was then stirred with IRA 400 (HO^-) resin for 10 min. The mixture was diluted with diethyl ether (20 mL), the resin was filtered off and the solution concentrated. The resulting syrup was purified by chromatography as usual (2:3 ethyl acetate-light petroleum) to give the title compound as a colorless oil (0.17 g, 94%); $[\alpha]_D$ −44° (*c* 0.7, dichloromethane); IR 3488 (OH), 2114 (N_3), 1747 cm^{-1} (CO ester); ^1H NMR ($CDCl_3$, 200 MHz), δ 4.17 (d, 1 H, $J_{2,3}$ 4.2 Hz, H-2), 3.91 (m, 1 H, H-5), 3.81 (s, 3 H, $COOCH_3$), 3.64 (dd, 1 H, $J_{3,4}$ 7.9 Hz, H-3), 3.53 (d, 2H, H-6, H-6′), 3.41 (dd, 1 H, $J_{4,5}$ 7.1 Hz, H-4), 3.51, 3.47, 3.41 (3s, each 3 H, OCH_3); ^1H (Me_2SO-d_6, 200 MHz), δ 5.19 (d, 1 H, $J_{OH,5}$ 5 Hz, OH), 4.16 (d, 1 H, $J_{2,3}$ 3.6 Hz, H-2), 3.91 (m, 1 H, H-5), 3.70 (s, 3 H, $COOCH_3$), 3.64 (dd, 1 H, $J_{3,4}$ 9.2 Hz, H-3), 3.40 (m, 1 H,

H-4), 3.45 (dd, 1 H, $J_{5,6}$ 5.9, $J_{6,6'}$ 9.5 Hz, H-6), 3.34 (dd, 1 H, $J_{5,6'}$ 5.5 Hz, H-6′), 3.38, 3.36, 3.25 (3s, each 3 H, OCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz), δ 170.94 (C-1), 80.32 (C-2), 79.47 (C-6), 72.90 (C-4), 70.41 (C-5), 62.50 (C-3), 59.43, 59.08, 58.98 (3 OCH_3), 52.21 ($COO\underline{C}H_3$).

Anal. Calcd for $C_{10}H_{19}N_3O_6$: C, 43.22; H, 6.90; N, 15.16. Found: C, 43.22; H, 6.87; N, 15.07.

Treatment of lactone 13 with trimethyl orthoformate: Isolation of 14. *Method a)*: A solution of lactone **13** (0.05 g, 0.2 mmol) in methanol (0.2 mL) containing trimethyl orthoformate (0.04 mL, 0.4 mmol) and concentrated H_2SO_4 (1.1 μL, 2.0×10^{-3} mmol), was heated at 50°C for 14 h. The solution was concentrated and the residue was solved in ethyl acetate (15 mL), washed with aq $NaHCO_3$ satd solution, dried (anhydrous $MgSO_4$) and concentrated. Flash-column chromatography of the residue (1:1 ethyl acetate-light petroleum) gave **14** (0.02 g, 35%).

Method b): Lactone **13** (0.05 g, 0.2 mmol) was solved in a solution of 0.11 M trifluoromethanesulfonic acid in methanol (0.06 mL) and trimethyl orthoformate (45μL, 0.4 mmol) was added. The mixture was stirred at room temperature overnight, then work-up as described for a) afforded **14** (0.03 g, 59%).

Treatment of 14 with MeI/NaH: Isolation of methyl 2,4,6-tri-*O*-methyl-D-*erythro*-(*Z*)-2-hexenoate (17), methyl 2,4,5,6-tretra-*O*-methyl-D-*erythro*-(*Z*)-2-hexenoate (18), and methyl 2,4,5,6-tetra-*O*-methyl-D-*erythro*-(*E*)-2-hexenoate (19). To sodium hydride (60%) (0.02 g, 0.58 mmol) washed with pentane (15 mL × 3) under an argon atmosphere, was added dropwise a solution of **14** (0.1 g, 0.36 mmol) in dry DMF (5 mL). The mixture was stirred at room temperature for 10 min, then MeI (75 μL, 1.2 mmol) was added and stirring was continued under the same conditions for 6 h. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and the organic solution was washed with 0.5 M HOAc:NaOAc (pH 4.74) (10 mL × 2), then with H_2O (10 mL) and dried (anhydrous Na_2SO_4). The solvent was evaporated under reduced pressure and the residue (0.17 g) showed a complex mixture of products on TLC. Flash-column chromatography of this residue using 1:5 to 2:3 ethyl acetate-light petroleum, afforded the following fractions: **15** (0.015 g, 20%), **17** (0.014 g, 18%), **18** (0.03 g, 33%), and **19** (0.025 g, 28%).

Compound **17**: IR 3507 (OH), 3080 (C=C-H), 1651 (C=C), 1728 cm^{-1} (CO ester); ^1H NMR ($CDCl_3$, 200 MHz), δ 6.10 (d, 1 H, $J_{3,4}$ 9.4 Hz, H-3), 4.24 (dd, 1 H, $J_{4,5}$ 5.0 Hz, H-4), 3.88 (bm, 1H, H-5), 3.79 (s, 3 H, $COOCH_3$), 3.46 (dd, 1H, $J_{5,6}$ 4.2, $J_{6.6'}$ 9.8 Hz, H-6), 3.35 (dd, 1H, $J_{5,6'}$ 6.8 Hz, H-6′), 3.69, 3.36, 3.29 (3s, each 3 H, OCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz), δ 163.29 (C-1), 149.19 (C-2), 123.20 (C-3), 75.7, 71.9 (C-4/C-5), 73.01 (C-6), 60.08, 59.13, 56.96 (3 OCH_3), 52.96 ($COO\underline{C}H_3$); MS (FAB): *m/z* 257 $(M + Na)^+$.

Compound **18**: IR 3144 (C=C-H), 1657 (C=C), 1728 cm^{-1} (CO ester); ^1H NMR ($CDCl_3$, 200 MHz), δ 6.10 (d, 1 H, $J_{3,4}$ 9.4 Hz, H-3), 4.32 (dd, 1 H, $J_{4,5}$ 3.7 Hz, H-4), 3.77 (s, 3 H, $COOCH_3$), 3.50−3.30 (m, 3H, H-5, H-6, H-6′), 3.68, 3.45, 3.33, 3.27 (4s, each 3 H, OCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz), δ 163.40 (C-1),

148.67 (C-2), 123.83 (C-3), 82.1, 75.2 (C-4/C-5), 71.80 (C-6), 60.02, 59.15, 58.81, 57.14 (4 OCH_3), 52.10 ($COO\underline{C}H_3$); MS (FAB): *m/z* 271 $(M + Na)^+$.

Compound **19**: ^1H NMR ($CDCl_3$, 200 MHz), δ 6.08 (d, 1 H, $J_{3,4}$ 9.0 Hz, H-3), 4.78 (dd, 1 H, $J_{4,5}$ 2.9 Hz, H-4), 3.80 (s, 3 H, $COOCH_3$), 3.55-3.35 (m, 3H, H-5, H-6, H-6′), 3.62, 3.49, 3.31, 3.29 (4s, each 3 H, OCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz), δ 163.34 (C-1), 148.08 (C-2), 109.52 (C-3), 82.60, 76.32 (C-4/C.5), 72.32 (C-6), 59.04, 58.69, 56.84, 55.51 (4 OCH_3), 52.17 ($COO\underline{C}H_3$); MS (FAB): *m/z* 271 $(M + Na)^+$.

Treatment of 14 with MeI/Ag_2O. a) Isolation of 3-deoxy-2,4,6-tri-*O*-methyl-D-*erythro*-hex-2-enono-1,5-lactone (15). To a solution of **14** (0.08 g, 0.3 mmol) in dry THF (1 mL) was added silver oxide (0.076 g, 0.33 mmol) and MeI (0.04 mL, 6 mmol) and the mixture was stirred at room temperature under argon for 5 h. The mixture was diluted with acetonitrile and the suspension was filtered through diatomaceous earth. The filtrate was concentrated and the residue was purified by flash-column chromatography (1:5 to 1:3 ethyl acetate-light petroleum) to give **15** (0.052 g, 87%) as an oil; $[\alpha]_D$ +84° (*c* 2.0, dichloromethane); IR 3073 (C=CH), 1753 (C=O lactone), 1655 cm^{-1} (C=C); ^1H NMR ($CDCl_3$, 200 MHz), δ 5.65 (d, 1 H, $J_{3,4}$ 4.1 Hz, H-3), 4.45 (dt, 1 H, $J_{4,5}$ 6.1 Hz, H-5), 4.23 (dd, 1 H, H-4), 3.64 (dd, 1 H, $J_{5,6}$ 4.1, $J_{6,6'}$ 10.7 Hz, H-6), 3.55 (dd, 1 H, $J_{5,6'}$ 4.6 Hz, H-6′), 3.67, 3.41, 3.37 (3s, each 3 H, OCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz), δ 159.47 (C-1), 145.21 (C-2), 107.21 (C-3), 79.42, 71.16 (C-4/C-5), 70.81 (C-6), 59.44, 56.62, 55.57 (3 OCH_3); HRMS (EI) Calcd for $C_9H_{14}O_5$: 202.084124. Found: 202.084455.

b) Isolation of methyl 3-azido-3-deoxy-2,4,5,6-tetra-*O*-methyl-D-altronate (16). A solution of **14** (0.06 g, 0.21 mmol) in dry acetonitrile (1 mL) was stirred with silver oxide (0.23 g, 0.42 mmol) and MeI (0.6 mL, 2.74 mmol) at 60°C for 60 h. A complex mixture of compounds was observed (TLC) and after working up as usual, the following compounds were isolated: **13** (0.014 g, 13%), **15** (0.05 g, 58%) and **16** (0.02 g, 17%) as a colorless oil; $[\alpha]_D$ −33° (*c* 1.2, dichloromethane); IR 2112 (N_3), 1755 cm^{-1} (CO ester); ^1H NMR ($CDCl_3$, 200 MHz), δ 4.09 (d, 1 H, $J_{2,3}$ 3.6 Hz, H-2), 3.77 (s, 3 H, $COOCH_3$), 3.73 (dd, 1 H, $J_{3,4}$ 9.2 Hz, H-3), 3.66-3.40 (m, 4 H, H-4, H-5, H-6, H6′), 3.47, 3.44, 3.42, 3.34 (4s, each 3 H, OCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz), δ 171.00 (C-1), 80.45, 79.95, 78.21 (C-2/ C-4/ C-5), 71.26 (C-6), 62.77 (C-3), 59.57, 59.06, 59.05, 58.42 (4 OCH_3), 52.10 ($COO\underline{C}H_3$); MS (CI): *m/z* 247 $(M + H - COOCH_3)^+$, 232 $(M - COOCH_3)^+$, 101 $(C_5H_9O_2)^+$.

Anal. Calcd for $C_{11}H_{21}N_3O_6$: C, 45.36; H, 7.27; N, 14.42. Found: C, 45.30; H, 7.01; N, 14.24.

c) A solution of **14** (0.11 g, 0.41 mmol) in dry acetonitrile (1 mL) was stirred with silver oxide (0.19 g, 0.8 mmol) and MeI (1.3 mL, 20.7 mmol) at room temperature for 7 days. Work- up as usual afforded **16** (23%) and **13** (21%).

d) To a solution of **14** (0.4 g, 1.4 mmol) in dry acetonitrile (7.5 mL) were added Dowex 50 × 8 resin (0.29 g, 1.44 meq H^+), molecular sieves 3 Å (0.4 g),

silver oxide (0.33 g, 1.44 mmol) and MeI (1.8 mL, 28.8 mmol). The mixture was heated, with stirring under argon, at 80°C for 10 h. During this time, more silver oxide (0.33 g, 1.44 mmol) and MeI (0.36 mL, 7.75 mmol) were added, then the mixture was diluted with acetonitrile (5 mL) and stirring was continued at 30°C overnight. Work-up as usual gave **16** (24%) and **13** (20%).

Methyl 3-amino-3-deoxy-2,4,6-tri-*O*-methyl-α-D-*altro*-hexopyranoside (20). Compound **20** was obtained from **11** (0.36 g, 1.38 mmol) as described above for the preparation of **7** and obtained as a colorless oil (0.30 g, 93%); $[\alpha]_D$ +98° (*c* 1.63, dichloromethane); IR 3440, 1632 cm^{-1} (NH_2); ^1H NMR ($CDCl_3$, 500 MHz), δ 4.55 (bs, 1 H, H-1), 3.90-3.75 (m, 2 H, H-3, H-5), 3.65 (dd, 1 H, $J_{5,6}$ 2.5, $J_{6,6'}$ 10.4 Hz, H-6), 3.57 (dd, 1 H, $J_{5,6'}$ 5.6, H-6′), 3.60−3.50 (m, 1 H, H-4), 3.45-3.35 (m, 1 H, H-2), 3.29, 3.28, 3.26, 3.23 (4s, each 3 H, OCH_3), 1.8 (bs, 2 H, NH_2); ^{13}C NMR ($CDCl_3$, 125 MHz), δ 99.32 (C-1), 79.60 (C-4), 74.35 (C-2), 72.05 (C-6), 65.73 (C-5), 59.35, 57.84, 56.60, 54.98 (4 OCH_3), 48.05 (C-3); MS (CI): *m/z* 236 $(M + H)^+$, 204 $(M - OCH_3)^+$, 172 $(M - CH_3OH - OCH_3)^+$; HRMS (EI) Calcd for $C_{10}H_{21}NO_5$: 235.1414. Found: 235.1418.

3-Amino-3-deoxy-2,4,6-tri-*O*-methyl-α,β-D-*altro*-hexopyranose (21). A solution of **20** (0.5 g, 2.2 mmol) in a 5:1 mixture of 4M HCl-acetonitrile (20 mL) was heated at 80°C for 2 h. The mixture was concentrated to dryness and extracted with CH_2Cl_2 (20 mL). The extract was washed with aq $NaHCO_3$ satd solution (10 mL × 2), dried (anhydrous $MgSO_4$) and concentrated to dryness. The residue (0.45 g) was purified by flash-column chromatography (10:1 CH_2Cl_2-MeOH) to give **21** as a solid (0.40 g, 85%), mp 174°C (dec.); $[\alpha]_D$ −73° (*c* 0.52, dimethyl sulfoxide); IR 3413, 1665 cm^{-1} (NH_2); ^1H NMR (Me_2SO-d_6, 500 MHz), α anomer: δ 5.00 (bs, 1 H, H-1), 4.36 (bs, 1 H, OH), 4.12 (ddd, 1 H, *J* 2.4, *J* 5.0, *J* 6.0 Hz, H-5), 4.05 (m, 1 H, H-3), 3.55 (m, 1 H, H-4), 3.36 (m, 2 H, H-6, H-6′), 3.30 (dd, 1 H, *J* 2.5, *J* 5.0 Hz, H-2); β anomer: δ 4.85 (bs, 1 H, H-1), 4.05 (m, 1 H, H-3), 4.01 (bs, 1 H, OH), 3.77 (ddd, 1 H, *J* 2.4, *J* 4.5, *J* 9.0 Hz, H-5), 3.55 (m, 1 H, H-4), 3.36 (m, 2 H, H-6, H-6′), 3.27 (dd, 1 H, *J* 1.9, *J* 4.2 Hz, H-2); α and β anomers: δ 3.46, 3.45, 3.37, 3.36, 3.35, 3.34 (6s, each 3 H, OCH_3); ^{13}C NMR (Me_2SO-d_6, 125 MHz), α anomer: δ 92.12 (C-1), 78.30 (C-2), 74.64 (C-4), 71.55 (C-6), 67.03 (C-5), 57.95 (C-3); β anomer: δ 91.22 (C-1), 78.57 (C-2), 74.54 (C-4), 72.15 (C-5), 71.48 (C-6), 57.14 (C-3); α and β anomers: δ 59.07, 58.99, 58.14, 57.95, 57.53, 57.14 (6 OCH_3).

Anal. Calcd for $C_9H_{19}NO_5$: C, 48.84; H, 8.66; N, 6.33. Found: C, 49.12; H, 8.30; N, 6.51.

3-(Benzyloxycarbonyl)amino-3-deoxy-2,4,6-tri-*O*-methyl-α,β-D-*altro*-hexopyranose (22). To a cold solution (0=n5°C) of **21** (0.26 g, 1.17 mmol) in aq $NaHCO_3$ satd solution (10 mL), benzyloxycarbonyl chloroformate (0.25 mL, 2.0 mmol) was added dropwise with stirring. The mixture was stirred at room temperature overnight, then H_2O was added (10 mL) and the mixture was extracted with $CHCl_3$ (25 mL × 3). The organic solution was washed with brine (25 mL),

dried (anhydrous $MgSO_4$) and concentrated to a residue (0.55 g). Flash-column chromatography of this residue (1:1 to 4:1 diethyl ether-light petroleum) afforded **22** as a white solid (0.2 g, 50%), mp 106–107°C; $[\alpha]_D$ +64° (*c* 0.87, dichloromethane); IR 3426 (NH and OH), 2990 (Ph), 1683 (NH-CO-O), 762, 695 cm^{-1} (Ph); ^1H NMR ($CDCl_3$, 500 MHz), α anomer: δ 7.37–7.26 (m, 5 H, Ph), 6.05 (d, 1 H, $J_{NH,3}$ 9.7 Hz, NH), 5.15 (dd, 2H, *J* 12.3 Hz, C$\underline{H}_2$-Ph), 5.21 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.49 (bd, 1 H, H-3), 4.04 (ddd, 1 H, $J_{4,5}$ 9.7, $J_{5,6}$ 2.2, $J_{5,6'}$ 7.2 Hz, H-5), 3.67 (dd, 1 H, $J_{6,6'}$ 10.2 Hz, H-6), 3.54 (dd, 1 H, H-6′), 3.42 (dd, 1 H, $J_{2,3}$ 1.5 Hz, H-2), 3.40 (m, 1 H, H-4), 3.44, 3.37, 3.36 (3s, each 3 H, OCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz), α anomer: δ 156.39 (C=O), 128.05–136.48 (Ph), 92.32 (C-1), 78.37 (C-4), 73.02 (C-2), 72.44 (C-6), 66.80 (C$\underline{H}_2$-Ph), 66.39 (C-5), 59.13, 58.05, 57.19 (3 OCH_3), 46.20 (C-3); MS (CI): *m/z* 338 $(M - NH_3)^+$, 248 $(M - PhCH_2O)^+$, 230 $(M - PhCH_2O - H_2O)^+$, and 91 $(Ph\text{-}CH_2)^+$.

Anal. Calcd for $C_{17}H_{25}NO_7$: C, 57.46; H, 7.09; N, 3.94. Found: C, 57.45; H, 7.05; N, 3.74.

3-(Benzyloxycarbonyl)amino-3-deoxy-2,4,6-tri-*O*-methyl-D-altrono-1,5-lactone (23). Compound **22** (0.4 g, 1.13 mmol) was oxidized to lactone **23** as described above for the preparation of **10**. Lactone **23** was a colorless oil (0.35 g, 87% yield); $[\alpha]_D$ +64° (*c* 0.87, dichloromethane); IR 3420 (NH), 1727 (CO lactone), 745, 699 cm^{-1} (Ph); ^{13}C NMR ($CDCl_3$, 125 MHz), δ 169.29 (C-1), 155.90 (C=O), 135.22, 128.57, 128.28, 128.16 (Ph), 77.87, 76.38, 76.25 (C-2/C-4/C-5), 72.03 (C-6), 67.12 (C$\underline{H}_2$-Ph), 59.55, 58.54, 57.82 (3 OCH_3), 50.34 (C-3); MS (CI): *m/z* 354 $(M + H)^+$ and 91 $(Ph\text{-}CH_2)^+$; HRMS (EI) Calcd for $C_{17}H_{23}NO_7$: 353.1468. Found: 353.1490.

3-Amino-3-deoxy-3,5-*N,O*-carbonyl-2,4,6-tri-*O*-methyl-D-altronic acid (24). To a solution of lactone **23** (0.11 g, 0.31 mmol) in dry THF (3 mL) was added freshly powdered KOH (0.07 g, 1.27 mmol), 18-crown-6 (8.4 mg, 10% mol) and MeI (0.07 mL, 1.0 mmol). The mixture was stirred in the dark at room temperature under argon for 3 h. Then CH_2Cl_2 (10 mL) was added and the solution was washed with H_2O (5 mL). The aqueous phase was treated with concentrated HCl to pH 2, then extracted with CH_2Cl_2 (15 mL × 4), dried (anhydrous $MgSO_4$) and concentrated to a residue (0.03 g). The aqueous phase was concentrated to dryness and extracted with MeOH. Evaporation of the methanol solvent gave a residue which was purified by flash-column chromatography, and the cyclic urethane **24** was isolated as a white solid (0.05 g, 60%), mp 118°C (dec); $[\alpha]_D$ −44° (*c* 0.69, methanol); IR 3336 (COOH), 1703 cm^{-1} (CO acid); ^1H NMR (Me_2SO-d_6, 200 MHz), δ 6.85 (bs, 1 H, NH), 4.25–3.40 (m, 6 H, sugar moiety), 3.33, 3.32, 3.27 (3s, each 3 H, OCH_3); ^{13}C NMR (Me_2SO-d_6, 50 MHz), δ 172.04 (COOH), 154.20 (CO, urethane), 79.28, 77.50, 71.49 (C-2/C-4/C-5), 70.34 (C-6), 60.06, 59.14, 58.85 (3 OCH_3), 57.12 (C-3); MS (CI): *m/z* 264 $(M + H)^+$, 220 $(M + H - CO_2)^+$.

Anal. Calcd for $C_{10}H_{17}NO_7$: C, 45.79; H, 6.15; N, 5.34. Found: C, 45.70; H, 6.22; N, 5.20.

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REFERENCES

1. Muñoz-Guerra, S.; López-Carrasquero, F.; Fernández-Santín, J.M.; Subirana, J.A. in *The Polymeric Materials Encyclopedia*; CRC Press: Boca Raton, Fl, 1996; Vol. 6, 4694–4700.
2. a) Seebach, D.; Ciceri, P. E.; Overhand, M.; Jaun, B.; Rigo, D; Oberer, L.; Hommel, U.; Amstutz, R.; Widmer, H. Probing the Helical Secondary Structure of Short-Chain β-Peptides. Helv. Chim. Acta **1996**, *79* (8), 2043–2066. b) Appella, D. H.; Christianson, L. A.; Karle, I. L.; Powell, D. R.; Gellman, S. H. β-Peptide Foldamers: Robust Helix Formation in a New Family of β-Amino Acid Oligomers. J. Am. Chem. Soc. **1996**, *118* (51), 13071–13072.
3. Eisenbach, C. D.; Lenz, R. W.; Duwal, M.; Marchessault, R. H. Polymerization of α,α-Disubstituted β-Propiolactones and Lactams, 12. Properties and Crystalline Structure of Poly(β-propiolactam)s. Makromol. Chem. **1979**,*180* (2), 429–440.
4. Thiem, J.; Bachmann, F. Carbohydrate-derived Polyamides. Trends Polym. Sci. **1994**, *2* (12), 425–432.
5. García-Martín, M. G.; de Paz Báñez, M. V.; Galbis, J. A. Preparation of 3-Amino-3-deoxy-2,4,5,6-tetra-*O*-methyl-D-altronic Acid Hydrochloride, a Precursor in the Preparation of a Chiral β-Polyamide (Nylon 3 Analog). J. Carbohydr. Chem. **2000**, *19* **(7)**, 805–815.
6. García-Martín, M. G.; de Paz Báñez, M. V.; Galbis, J. A. Preparation of 2-Amino-2-deoxy-3,4,5,6-tetra-*O*-methyl-D-gluconic Acid Hydrochloride, an Intermediate in the Preparation of Polypeptide-type Polyamides. Carbohydr. Res. **1993**, *240*, 301–305.
7. Bueno Martínez, M.; Zamora Mata, F.; Ugalde Donoso, M. T.; Galbis, J. A. Some Derivatives of 6-Amino-6-deoxy-D-gluconic Acid that are Precursors for the Synthesis of Polyamides. Carbohydr. Res. **1992**, *230*, 191–195.
8. Lederkremer, R. M.; Litter, M. I.; Sala, L. F. β-Elimination in Aldonolactones: a Convenient Synthesis of 2,4,6-Tri-*O*-benzoyl-3-deoxy-D-*arabino*-hexono-1,5-lactone. Carbohydr. Res. **1974**, *36*, 185–187.
9. Varela, O.; Fernández Cirelli, A.; Lederkremer, R. M. β-Elimination in Aldonolactones: Synthesis of 3,6-Dideoxy-L-*arabino*-hexose (Ascarylose). Carbohydr. Res. **1979**, *70*, 27–35.
10. Hoos, R.; Naughton, A. B.; Vasella, A. A Convenient Procedure for the Synthesis of 2,3,4,6-Tetra-*O*-benzyl-D-gluconolactam and D-Nojirilactam. Helv. Chim. Acta **1992**, *75*, 1802–1807.
11. Zamora, F.; Galbis, J. A. Synthesis of 3-Deoxy-2,4-di-*O*-methyl-D-erythro-pentono-1,5-lactone and its L Enantiomer by Stereoselective Hydrogenation of α,β-Unsaturated Aldono-1,5-lactones. Carbohydr. Res. **1996**, *293*, 251–258.

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