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Note

Synthesis of D-2-(2,3-dideoxy-D-*ribo* [and *arabino*]-hexopyranos-3-yl)glycine derivatives*

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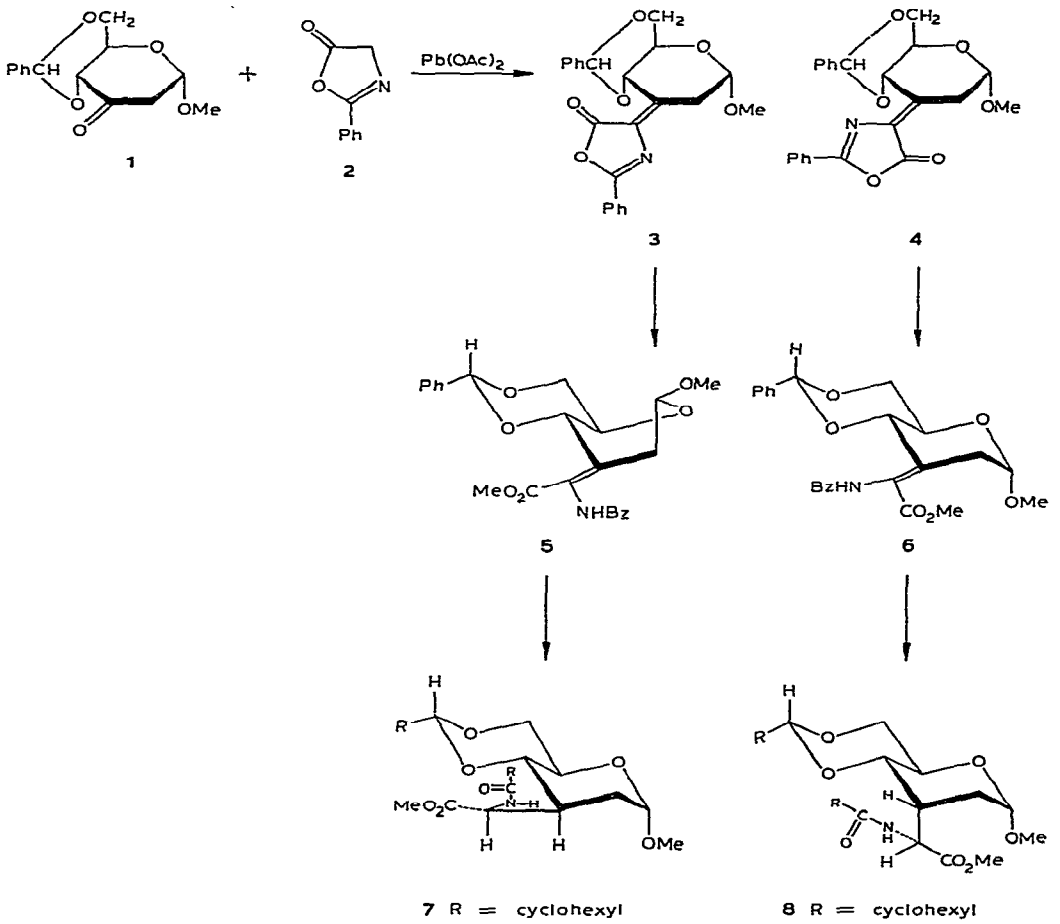
In continuation of our studies on the synthesis of *C*-carbohydrate α-amino acids[1,2] we now report an extension of the azlactone synthesis of amino acids[3] to a 2-deoxy-3-ketose (**1**) to yield 2,3-dideoxy branched-chain glycos-3-yl α-amino acids. In our previous communication[1] we reported that condensation of 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose with preformed 2-phenyl-oxazolin-5-one in the presence of 0.3 mol of anhydrous lead(II) acetate in refluxing 1,2-dimethoxyethane for 24 h afforded a 1:1 mixture of (*E*)- and (*Z*)-4-(1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ylidene)-2-phenyl-2-oxazolin-5-one in 75% yield. Similar treatment of methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose[4] (**1**) with 2-phenyl-2-oxazolin-5-one (**2**) afforded a very low yield of product. However, when the condensation was conducted for 2 h in the presence of a five-fold increase in the amount of catalyst, the yield of product was greatly increased. Chromatography of the product on silica gel with 97:3 benzene–ethyl acetate as developer afforded crystalline (*E*)-4-(methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hexopyranosid-3-ylidene)-2-phenyl-2-oxazolin-5-one (**3**) and the *Z* isomer (**4**) in 13 and 27% yields, respectively. Interestingly both geometrical isomers were obtained from the 2-deoxy-3-ketose reported herein and from the glycos-3-ulose reported previously[1], whereas an anhydro aldose[2] yielded only one azlactone. It has been observed previously[5] that sometimes the azlactone synthesis affords only one of the two possible geometric isomers. The n.m.r. spectra of a number of isomeric azlactones, and of the methyl benzamido-acrylates derived from the corresponding azlactones, have been investigated[6–8]. In each case it was found[6] that the methoxycarbonyl group of the acrylates deshields the *cis*-related γ-proton by up to 0.4 p.p.m. It was also determined that the *N*-benzoyl group exerts little, if any, effect on the γ protons. Thus, as H-2e of compound **4** resonates at lower field than H-2e of compound **3** (3.72 *vs* 3.28), the structures of the azlactones were assigned as shown. Methanolysis of compounds

*2-Deoxyglycosyl α-Amino Acids, Part VI.



3 and 4 with a catalytic amount of sodium acetate in methanol, which should not change the geometric configuration[5,8], gave a quantitative yield of methyl (*E*)-3-*C*-[benzamido(methoxycarbonyl)methylene]-4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hexopyranoside (**5**) and the *Z* isomer **6**. The greater deshielding effect exerted by the methoxycarbonyl group on H-2e than on H-2a (δ 2.91 *vs* 2.46) of compound **6** is as expected[4], and thus confirms the structure of compound **4**. On the other hand, H-2e and H-2a of **5** resonate at about δ 2.7 and appear almost as the AB portion of an ABX system. This evidence tentatively suggests that compound **5** probably exists in a deformed-boat conformation. Such a conformation might be expected, because of steric repulsion between the benzamido group on the chain branch and the methoxyl group at C-1. Undoubtedly, there is also steric repulsion between the methoxycarbonyl group and the benzylidene acetal group. Hydrogenation of compound **5** over 5% rhodium-on-alumina afforded compound **7** (71% yield) and an unknown compound; these were separated by chromatography on silica gel using 4:1 hexanes–acetone as developer. In compound **7**, the phenyl rings of the benzylidene and benzamido

groups were reduced to cyclohexylidene rings, as indicated by both elemental analysis and p.m.r. spectra.

The p.m.r. spectrum of the fully reduced derivative **7** (see Experimental section) is readily analyzed and can be used to deduce the structure of the branched-chain glycosyl amino acid **7**. Because high-field signals are generally attributed to hydrogen atoms attached to carbon atoms that have no oxygen atoms attached to them[9], it may be assumed that the multiplet of peaks corresponding to one proton at δ 2.62 arises from H-3. Irradiation at δ 2.62 collapsed the quartet at δ 4.88 to a doublet having a coupling constant of 5.3 Hz. The quartet at δ 4.88 showed two doublets, one having J 5.3 and the other J 9.8 Hz. As irradiation at δ 2.62 should remove the multiplicities due to coupling to H-3, the unaffected splitting (5.3 Hz) may be attributed to $J_{4,5}$ coupling, whereas the larger (J 9.8 Hz) coupling constant, which is thus removed must be attributed to coupling between H-4 and H-3 in a *trans*-diaxial orientation. It then follows that the C-3 chain-branch must be in equatorial orientation, and the sugar moiety of **7** must have the *arabino*-configuration.

Because the stereochemistry of catalytic hydrogenation is *cis*, it was surmised that hydrogen must have added to the exocyclic, carbon-carbon double-bond from the α-face of the pyranose ring of compound **5**, whence the configuration of the chiral carbon of the glycine moiety must be *D*. This hypothesis was confirmed by circular-dichroism measurements on compound **7**. Compound **7** exhibited an intense, negative Cotton effect, in agreement with the negative Cotton effect shown by other similarly constituted D-amino acids[10,11]. The faster-moving compound, obtained in 9% yield from the reduction of **5**, had not suffered reduction of the phenyl rings (as evidenced by elemental and n.m.r. analyses). First-order analysis of the n.m.r. spectrum of this compound did not reveal the H-4 resonance. The H-2a and H-2e resonances were narrow, with base shoulders of 11 Hz. Irradiation at δ 4.8 (H-1) simplified H-2e and H-2a resonances. The narrowness of the H-2e and H-2a resonances suggests that H-3 is equatorial and therefore this compound had the *ribo* configuration.

Hydrogenation of compound **6** over 5% rhodium-on-powdered alumina yielded crystalline compound **8** in 68% yield. As in the structure proof of compound **7**, the structure of **8** was assigned from its n.m.r. spectrum. Thus, as H-2a of **8** resonates as an octet at δ 2.33 with $J_{1,2a}$ 4.5, $J_{2e,2a}$ 14.5, and $J_{2a,3}$ 0.9 Hz (irradiation at δ 4.65 collapsed the octet to a quartet with $J_{2a,2e}$ 14.5 and $J_{2a,3}$ 0.9 Hz), it was surmised that H-3 must be equatorially oriented. Irradiation at δ 4.65 also collapsed the H-2e quartet to a doublet having $J_{2a,2e}$ 14.5 Hz. As no H-2e,3 coupling was discernible, this evidence corroborated the hypothesis that H-3 must be in equatorial orientation. Therefore, compound **8** must have the *ribo* configuration. From this assignment, it follows that hydrogen must have added from the β face of the sugar[4], and the configuration of the amino acid moiety must be D. The latter supposition was corroborated by the fact that compound **8** exhibited an intense, negative Cotton-effect[10,11]. Therefore, compound **9** must be methyl *N*-cyclohexylcarbonyl-D-2-(methyl 4,6-*O*-cyclohexylmethylidene-2,3-dideoxy-α-D-*ribo*-hexopyranosid-3-yl)glycinate. Interestingly, catalytic hydrogenation of (*Z*)-methyl 4,6-*O*-benzylidene-3-*C*-

(carbomethoxymethylidene)-2,3-dideoxy-α-D-*erythro*-hexopyranoside followed a similar stereochemical course, yielding exclusively the *ribo* branched-chain sugar[4].

When methyl *N*-cyclohexylcarbonyl-D-2-(methyl 4,6-*O*-cyclohexylmethylidene-2,3-dideoxy-α-D-*arabino*-hexopyranosid-3-yl)glycinate (**7**) was treated with 80% trifluoroacetic acid, it underwent loss of the 4,6-*O*-cyclohexylmethylidene group, followed by intramolecular cyclization to afford a 1′,4(-γ)-lactone. In addition, demethylation of the glycoside led to 1,6-anhydro ring-formation. Precedent for the latter supposition was found in our previous work[12], wherein it was found that treatment of methyl 4,6-*O*-benzylidene-3-*C*-(cyanomethyl)-2,3-dideoxy-α-D-*ribo*-hexopyranoside with Dowex-50W X-8 (H^+) resin led to the formation of 1,6-anhydro-3-*C*-(cyanomethyl)-2,3-dideoxy-α-D-*ribo*-hexopyranose. The molecular ion of the product, observed at *m/e* 295, coupled with n.m.r. and elemental analysis, supported the hypothesis that compound **7** was converted into D-2-(1,6-anhydro-2,3-dideoxy-D-*arabino*-hexopyranos-3-yl)-*N*-(cyclohexylcarbonyl)glycine 1′,4-lactone.

EXPERIMENTAL

General methods. — Solutions were dried with anhydrous sodium sulfate and evaporated under diminished pressure. Column chromatography was performed on t.l.c.-grade silica gel under a pressure of 4–8 lb.in^{-2} with flow rates of 70–140 ml/h. P.m.r. spectra were determined in chloroform-*d* solution with tetramethylsilane as the internal standard by using a Varian HA-100 spectrometer. Chemical shifts are reported in p.p.m. (δ) and signals are described as s (singlet, d (doublet), t (triplet), q (quartet), o (octet), and m (multiplet). Values given for coupling constants are first order. Optical rotations were measured with a Perkin–Elmer Model 141 automatic polarimeter. Circular-dichroism measurements were performed with a Jasco J-20 automatic recording spectropolarimeter at room temperature. Concentrations of solutions are expressed as mol. liter^{-1}. I.r. spectra were recorded with a Perkin–Elmer 337 spectrometer. All melting points are corrected. Elemental analyses were obtained by Mr. Borda of the Microanalytical Laboratory of the University of British Columbia.

(E)-*4-(Methyl 4,6-O-benzylidene-2,3-dideoxy-α-D-*erythro-*hexopyranosid-3-ylidene)-2-phenyloxazol-5-one* (**3**) *and its Z-isomer* **4**. — To a mixture of anhydrous methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose[4] (**1**, 2.6 g) and 2-phenyloxazol-5-one (**2**, 2.5 g) in anhydrous dimethoxyethane (500 ml) was added lead(II) acetate (2.0 g). The mixture, contained in an apparatus described previously[3], was heated under reflux in an atmosphere of nitrogen. After 2 h, the starting material was consumed (t.l.c., 19:1 benzene–ethyl acetate). After the addition of xylene (100 ml), the mixture was concentrated under diminished pressure to a volume of 100 ml. Benzene (200 ml) was added and the solution was sequentially washed with water (100 ml), 10% aqueous sodium hydrogencarbonate (2 × 100 ml), and water (100 ml). The organic layer was dried (sodium sulfate) and evaporated to a solid that was chromatographed on silica gel (200 g) with 97:3 benzene–ethyl

acetate as developer. Compound **3** (0.60 g, 13%) was first eluted, followed by compound **4** (1.3 g, 27%). Compound **3** was recrystallized from ether; m.p. 200–201°, $[\alpha]_D^{25}$ −193° (*c* 0.6 chloroform); R_F 0.53 (19:1 benzene–ethyl acetate); n.m.r. ($CDCl_3$); 7.3–8.1 (complex, 10, aromatic), 5.81 (s, 1, benzylidene), 4.90 (t, 1, $J_{1,2a} = J_{1,2e}$ 4.8 Hz, H-1), 4.70 (d.d., 1, $J_{2,4}$ 1.0 and $J_{4,5}$ 8.5 Hz, H-4), 3.85–4.52 (complex, 3, H-5, H-6) 3.41 (s, 3, CH_3), and 3.28, 3.10 (2dd, 2, $J_{1,2a} = J_{1,2e}$ 4.8, $J_{2,4}$ 1.0 Hz, H-2a, H-2e).

Anal. Calc. for $C_{23}H_{21}NO_6$: C, 67.81; H, 5.20; N, 3.44. Found: C, 67.68; H, 5.16; N, 3.25.

Compound **4** was recrystallized from ether; m.p. 227–228°, $[\alpha]_D^{25}$ +88.2° (*c* 1.6, chloroform); R_F 0.61 (19:1 benzene–ethyl acetate); n.m.r. ($CDCl_3$): 7.5–8.2 (complex, 10, aromatic), 5.88 (s, 1, benzylidene), 5.04 (dd, 1, $J_{1,2a} = J_{1,2e}$ 4.0 Hz, H-1), 5.0–5.8 (complex, 4, H-4, H-5, 2H-6), 4.50 (s, 3, CH_3), and 3.72, 3.56 (2d, 2, $J_{1,2a} = J_{1,2e}$ 4.0 Hz, H-2a, H-2e).

Anal. Calc. for $C_{23}H_{21}NO_6$: C, 67.81; H, 5.20; N, 3.44. Found: C, 67.50; H, 5.40; N, 3.27.

(E)-*Methyl* 3-C-[*benzamido*(*methoxycarbonyl*)*methylene*]-*4,6*-O-*benzylidene*-2,3-*dideoxy*-α-D-erythro-*hexopyranoside* (**5**). — Compound **3** (0.32 g) was dissolved in methanol (50 ml) containing sodium acetate (20 mg). After being kept for 3 h at 60° this solution was cooled, yielding crystalline compound **5** (0.33 g, 100%), m.p. 220–221°, $[\alpha]_D^{25}$ +185° (*c* 0.3, chloroform); n.m.r. ($CDCl_3$): 7.3–7.9 (complex, 10, aromatic), 5.60 (s, 1, benzylidene), 4.84 (t, 1, $J_{1,2a} = J_{1,2e}$ 3.7 Hz, H-1), 3.6–4.6 (complex, 4, H-4, H-5, 2H-6), 3.38 (2s, 6, CH_3 ester and ether), and 2.68 (m, 2, AB of ABX system, $J_{1,2}$ 3.7, $J_{2a,2e}$ 15 Hz, H-2e, H-2a).

Anal. Calc. for $C_{24}H_{25}NO_7$: C, 65.59; H, 5.73; N, 3.19. Found: C, 65.44; H, 5.74; N, 3.14.

(Z)-*Methyl* 3-C-[*benzamido*(*methoxycarbonyl*)*methylene*]-*4,6*-O-*benzylidene*-2,3-*dideoxy*-α-D-erythro-*hexopyranoside* (**6**). — Compound **4** (0.96 g) was hydrolyzed by the procedure just described to yield crystalline **6**; m.p. 183–184°, $[\alpha]_D^{25}$ +38.1° (*c* 0.5, chloroform); n.m.r. ($CDCl_3$): 9.50 (s, 1, exchanges in D_2O, N-H), 6.7–7.5 (complex, 10, aromatic), 5.52 (s, 1, benzylidene), 4.68 (m, 1, $J_{1,2a}$ 3.8, $J_{1,2e}$ 0.8 Hz, H-1), 3.9–4.5 (complex, 4, H-4, H-5, 2H-6), 3.82 (s, 3, CH_3 ester), 3.28 (s, 3, CH_3 ether), 2.91 (m, 1, $J_{1,2e}$ 0.8, $J_{2e,2a}$ 15 Hz, H-2e), and 2.46 (m, 1, $J_{1,2a}$ 3.8, $J_{2e,2a}$ 15 Hz, H-2a).

Anal. Calc. for $C_{24}H_{25}NO_7$: C, 65.59; H, 5.73; N, 3.19. Found: C, 65.38; H, 5.50; N, 3.21.

Methyl N-*cyclohexylcarbonyl*-D-*2*-(*methyl* 4,6-O-*cyclohexylmethylidene*-*2,3*-*dideoxy*-α-D-arabino-*hexopyranosid*-*3*-*yl*)*glycinate* (**7**). — Compound **5** (150 mg) in ethanol (100 ml) was hydrogenated with 5% rhodium-on-powdered alumina (80 mg) for 12 h at 5 atm and 35°. The catalyst was removed by filtration and the filtrate was evaporated to yield a solid product that was chromatographed on silica gel (15 g) with 4:1 hexanes–acetone as developer. The slower-moving compound **7** (115 mg, 71%) was recrystallized from acetone–hexanes; m.p. 141–142°, $[\alpha]_D^{25}$ +63.2° (*c* 1,

chloroform); c.d. $\Delta\varepsilon_{225}$ −1.6 (*c* 0.0022, methanol), $[\theta]^{30}_{225}$ −5280; n.m.r. ($CDCl_3$): 7.15 (broad s, 1, NH), 4.88 (q, 1, $J_{3,4}$ 9.8, $J_{4,5}$ 5.3 Hz, H-4), 4.64 (t, 1, $J_{1,2e} = J_{1,2a}$ 3.8 Hz, H-1), 4.24 (d, 1, *J* 4.2 Hz, methylidene), 3.3–4.2 (complex, 4), 3.72 (s, 3, CH_3 ester), 3.23 (s, 3, CH_3 ether), 2.62 (m, 1, $J_{2e,3}$ 3.8, $J_{2a,3}$ 11.0 Hz, $J_{3,4}$ 9.8 Hz, H-3), and 1.0–2.0 (complex, 24, H-2a, H-2e, cyclohexyl). Irradiation at δ 2.62 collapsed the quartet at δ 4.88 to a doublet having $J_{4,5}$ 5.3 Hz. Irradiation at δ 1.9 collapsed the triplet at δ4.74 and the doublet at δ 4.24 to singlets.

Anal. Calc. for $C_{24}H_{39}NO_7$: C, 63.55; H, 8.67; N, 3.09. Found: C, 63.28; H, 8.79; N, 3.06.

The faster-moving compound (15 mg, 9%) was recrystallized from acetone–hexanes; m.p. 186–188°, $[\alpha]^{25}_D$ +62.4° (*c* 0.2, chloroform); c.d. $\Delta\varepsilon_{225}$ −0.73 (*c* 0.0084, methanol), $[\theta]^{30}_{225}$ −2409; n.m.r. ($CDCl_3$): 7.81 (broad s, NH), 6.9–7.5 (complex, 10, aromatic H), 5.49 (s, 1, benzylidene), 5.11 (q, 1, $J_{1',3}$ 10, $J_{NH,1'}$ 4.8 Hz, H-1'), 4.64 (q, 1, $J_{1,2a}$ 3.8, $J_{1,2e}$ 2.4 Hz, H-1), 3.4–4.4 (complex, 4, H-4, H-5, 2H-6), 3.69 (s, 3, CH_3 ester), 3.29 (s, 3, CH_3 ether), 3.7 (m, 1, H-3), and 2.98 (m, 2, $J_{2a,3}$ 5.7 Hz, H-2a and H-2e). Irradiation at δ 4.64 changed the multiplet at δ2.98. Irradiation at δ 3.7 collapsed the quartet at δ 5.11 to a doublet ($J_{NH,1'}$ 4.8 Hz). Deuterium exchange of the amide proton at δ 7.81 collapsed the quartet at δ 5.11 to a doublet ($J_{1',3}$ 10 Hz).

Anal. Calc. for $C_{24}H_{27}NO_7$: C, 65.29; H, 6.17; N, 3.17. Found: C, 65.14; H, 6.53; N, 3.23. It is tentatively suggested, on the basis of the n.m.r. data, that the faster-moving compound is probably methyl *N*-benzoyl-L-2-(methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*ribo*-hexopyranosid-3-yl)glycinate.

Methyl N-*cyclohexylcarbonyl*-D-*2-(methyl 4,6*-O-*cyclohexylmethylidene-2,3-dideoxy*-α-D-ribo-*hexopyranosid-3-yl)glycinate* (**8**). — Compound **6** (150 mg) was hydrogenated in ethanol (100 ml) with 5% rhodium-on-powdered alumina (80 mg) for 36 h at 5 atm and 40°. Filtration and evaporation of the filtrate gave **8**, which was recrystallized from acetone–hexanes; yield 110 mg (68%), m.p. 127–130°, $[\alpha]^{25}_D$ +57.7° (*c* 0.7, chloroform); $\nu^{CHCl_3}_{max}$ 1739 (C = O of ester) and 1680 cm^{-1} (C = O of amide); $\Delta\varepsilon_{225}$ −2.2 (*c* 0.00043, in methanol), $[\theta]^{30}_{225}$ −7260, n.m.r. ($CDCl_3$): 4.65 (dd, 1, $J_{1,2a}$ 4.5, $J_{1,2e}$ 1.8 Hz, H-1), 4.37 (d, 1, *J* 4.6 Hz, methylidene), 4.31 (d, 1, $J_{2',3}$ 4.1 Hz), 3.35–4.2 (complex, 4, H-4, H-5, 2H-6), 3.78 (s, 3, CH_3 of ester), 3.29 (s, 3, CH_3 of ester), 2.77 (q, 1, $J_{1,2e}$ 1.8, $J_{2e,2a}$ 14.5 Hz, H-2e), 2.33 (o, $J_{1,2a}$ 4.5, $J_{2e,2a}$ 14.5, $J_{2a,3}$ 0.9 Hz, H-2a), and 1.0–2.0 (complex, 23, H-3 and cyclohexyl). Irradiation at δ 4.65 collapsed the quartet at δ 2.77 to a doublet having $J_{2a,2e}$ 14.5 Hz and collapsed the octet at δ 2.33 to a quartet having $J_{2a,2e}$ 14.5 Hz and $J_{2a,3}$ 0.9 Hz.

Anal. Calc. for $C_{24}H_{39}NO_7$: C, 63.55; H, 8.67; N, 3.09. Found: C, 63.54; H, 8.50; N, 3.02.

Column chromatography of the mother liquor with 1:4 acetone–hexanes as developer gave **8** and a small amount of a compound having one phenyl and one cyclohexyl ring.

Attempted hydrolysis of **7** *and* **8** *with barium hydroxide.* — The protected amino

acids **7** and **8** (20 mg) were each subjected to hydrolysis with barium hydroxide in aqueous ethanol. The amide group of each compound was totally resistant to hydrolysis.

D-*2-(1,6-Anhydro-2,3-dideoxy-β*-D-arabino-*hexofuranos-3-yl)*-N-*(cyclohexylcarbonyl)glycine 1',4-lactone.* — To a solution of compound **7** (18 mg) in dichloromethane (10 ml) was added 80% trifluoroacetic acid (1.0 ml). The solution was stirred for 20 h at room temperature. After the mixture had been evaporated to dryness, the product was azeotropically dried under diminished pressure with xylene (3 × 10 ml). Chromatography on a column to t.l.c.-grade silica gel (2.0 g, with 2:1 hexanes–acetone) afforded a crystalline product (6 mg) that was recrystallized from acetone–hexanes; m.p. 276–278, $[\alpha]_D^{25}$ +38.40 (*c* 0.2, chloroform); n.m.r. data (in $CDCl_3$): δ 5.55 (s, with shoulders, 1H, H-1), 4.9 (d, $J_{1',3}$ 8 Hz, H-1'), 4.50 (m, H-4), 3.9 (m, 3H), 2.5 (m, 1H, H-3), 1.9 (m, 2H, H-2e, H-2a), and 1.3–1.8 (m, cyclohexyl).

Anal. Calc. for $C_{15}H_{21}NO_5$ (295): C, 61.00; H, 7.17; N, 4.74. Found: C, 61.23; H, 7.06; N, 4.40; mol. wt. (by mass spectrometry), 295.

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