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Note

Chemical modification of some methyl (3,4-di-*O*-acetyl-2-deoxy-2-hydroxyimino-α-D-*arabino*-hexopyranosid)uronates

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Abstract

Methyl [ethyl 3,4-di-*O*-acetyl-2-deoxy-2-(*Z*)-hydroxyimino-α-D-*arabino*-hexopyranosid]-uronate (**1**) and *N*-*tert*-butoxycarbonyl-*O*-[methyl 3,4-di-*O*-acetyl-2-deoxy-2-(*Z*)-hydroxy-imino-α-D-*arabino*-hexo-pyranosyluronate]-L-serine methyl ester (**2**) were modified at C-2 and C-3. They have been transformed into the corresponding methyl (2,3,4-tri-*O*-acetyl-α-D-glycopyranosid)uronates by the sequence of reactions 2-C=N–OH → 2-C=O → 2-C–OH → 2-C–OAc. Reaction of **1** and **2** with sodium azide gave the corresponding methyl [ethyl 4-*O*-acetyl-3-azido-2,3-dideoxy-2-(*Z*)-hydroxyimino-α-D-glycopyranosid]uronates and *N*-*tert*-butoxycarbonyl-*O*-[methyl 4-*O*-acetyl-3-azido-2,3-dideoxy-2-(*Z*)-hydroxyimino-α-D-glycopyranosyluronate]-L-serine methyl esters.

Keywords: O-Glycosides; L-Serinate glycosides; Deoximation; Glycuronic acid; Azide derivatives; Conformation

The 2-deoxy-2-hydroxyimino derivatives of sugars are a versatile group of compounds that are very useful as starting reagents for the synthesis of modified sugars [1–9]. Previously we have reported the synthesis of some methyl 2-deoxy-2-hydroxyimino-D-*arabino*-hexopyranosiduronates of ethanol, L-serine, and pyrazole [10]. We now present the results of the chemical modification of some of these glycosides at C-2 and C-3 to establish the possibility of obtaining glycuronic acid analogues by this pathway.

Methyl [ethyl 3,4-di-*O*-acetyl-2-deoxy-2-(*Z*)-hydroxyimino-α-D-*arabino*-hexopyranosid]uronate (**1**) and *N*-*tert*-butoxycarbonyl-*O*-[methyl 3,4-di-*O*-acetyl-2-deoxy-2-(*Z*)-hydroxyimino-α-D-*arabino*-hexopyranosyluronate]-L-serine methyl ester (**2**) were modified at C-2 via the reaction sequence >C=N–OH → >C=O → >CHOH → >CHOAc. The deoximation of the hydroxyimino group was accomplished with acetaldehyde in the presence of hydrochloric acid [11] and the resulting ketone was reduced with sodium borohydride [12] and then acetylated. Thus **1** yielded exclusively methyl (ethyl 2,3,4-tri-*O*-acetyl-α-D-glucopyranosid)uronate (**3**); however, the appli-

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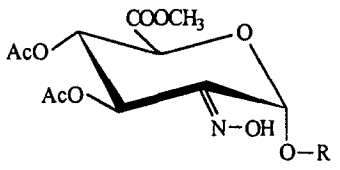
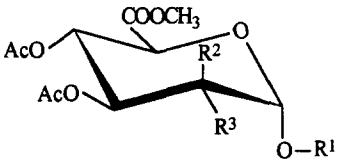
cation of this reaction sequence to **2** gave *N-tert*-butoxycarbonyl-*O*-(methyl 2,3,4-tri-*O*-acetyl-α-D-gluco- (**4**) and -α-D-manno-pyranosyluronate)-L-serine methyl ester (**5**), and methyl 2-acetoxyimino-1,3,4-tri-*O*-acetyl-2-deoxy-D-*arabino*-hexopyranuronate (**6**), in the ratios ~ 5:1:0.5.



1 R = C_2H_5

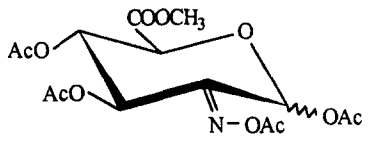
2 R = $CH_2-CH(NHBoc)-COOCH_3$



3 $R^1 = C_2H_5$, R^2 = H, R^3 = OAc

4 $R^1 = CH_2-CH(NHBoc)-COOCH_3$
R^2 = H, R^3 = OAc

5 $R^1 = CH_2-CH(NHBoc)-COOCH_3$
R^2 = OAc, R^3 = H



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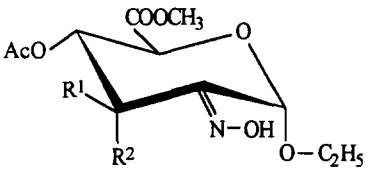
The result of deoximation and reduction of compound **1** is in full agreement with the influence of stereoelectronic interactions, in particular that of the anomeric carbon configuration, on the stereochemistry of reduction of hexopyranosid-2-uloses. It has been found that reduction of α anomers affords the product of axial approach of the hydride ion to C-2, whereas an equatorial approach is found with β anomers [6,13].

The smaller overall yield of the L-serinate glycosides (60%), as compared to that of the ethyl glycoside (75%), can be explained by partial cleavage of the *N-tert*-butoxycarbonyl group during deoximation which, in turn, caused higher solubility of this deprotected product, as well as by slight degradation of the glycosidic linkage as can be confirmed by the presence of **6** among the reaction products. This shows that the glycosidic linkage in **2** is weaker than in **1**.

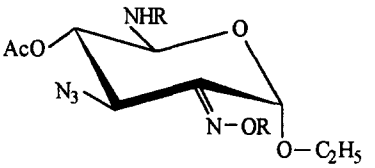
The structures of **3**, **4**, and **5** were established on the basis of the ^1H NMR data. The coupling constants $J_{1,2}$ 4 and $J_{2,3}$ 10 Hz give evidence of α-D-*gluco* structures for **3** and **4**. For compound **5**, the coupling constants $J_{1,2} = J_{2,3} = 3$ Hz reflect the α-D-*manno* configuration.

Compounds **1** and **2** were also modified at C-3. Upon reaction of these compounds with sodium azide in boiling ethanol, the 3-OAc group was replaced by the azide ion by the elimination–addition process [5,6,14,15]. The azido group was selected because it can, by reduction, afford aminoglycuronic acid precursors.



7 $R^1 = N_3$, R^2 = H

8 R^1 = H, $R^2 = N_3$



9 R = H

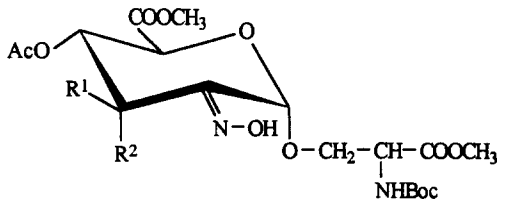
10 R = Ac

Thus, the reaction of **1** with NaN_3 gave **7**–**9** in the ratios 1:8:4 in ~ 65% overall yield. Compounds **7** and **8** are the products of equatorial (α-D-*arabino*, $J_{3,4} = J_{4,5} = 10$ Hz) and axial (α-D-*ribo*, $J_{3,4}$ 4, $J_{4,5}$ 10 Hz) 'displacement' of 3-OAc by the azide anion, respectively. The formation of ethyl (5*S*)-4-*O*-acetyl-5-amino-3-azido-2,3-dideoxy-2-hydroxyimino-α-D-*threo*-pentopyranoside (**9**) from **1** was unexpected and may be explained as follows. Not only the 'displacement' of the 3-OAc group by azide ion takes place, but also, to a small extent, the replacement by the N_3 group of OCH_3 in the ester fragment at C-5 to give the corresponding acid azide. This product then

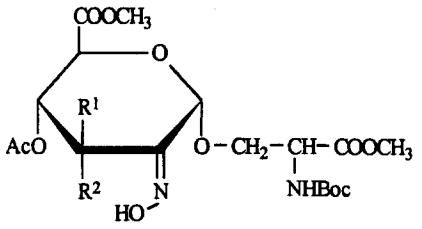
undergoes the Curtius rearrangement to give an isocyanate, which reacts with water to form the amine derivative **9**. The formation of **9** was quite unexpected since the reaction of sodium azide with carboxylic acid esters has not been employed as a method for the synthesis of acyl azides. Acetylation of **9** (Ac_2O–pyridine–DMAP) gave the (5*S*)-5-acetamido-2-acetoxyimino-3-azido-2,3-dideoxy-α-D-*threo* derivative **10**. The D-*threo* configuration of **9** and **10** was assigned on the basis of the values of $J_{3,4} = J_{4,5} = 10$ Hz.

Bearing in mind the δ values for the signals of H-1 in **7**–**9** (δ 6.15, 6.00, and 6.15, respectively) we assume that in these compounds the 2-hydroxyimino group has the same, probably *Z*, configuration.

On the other hand, the treatment of **2** with sodium azide gave four products, **11**–**14**,



11 $R^1 = N_3$, $R^2 = H$
12 $R^1 = H$, $R^2 = N_3$



13 $R^1 = N_3$, $R^2 = H$
14 $R^1 = H$, $R^2 = N_3$

in the ratios ~2:5:2:5 with an overall yield of ~62%.

The ^{1}H NMR data show that compounds **11** and **13** are the products of equatorial 'displacement' of the 3-OAc group by the azide ion (D-*arabino* isomer, $J_{3,4} = J_{4,5} = 10$ Hz for **11** and $J_{3,4} = J_{4,5} = 7$ Hz for **13**), whereas compounds **12** and **14** are the products of axial substitution (D-*ribo* isomer, $J_{3,4}$ 3, $J_{4,5}$ 9 Hz for **12** and $J_{3,4}$ 5, $J_{4,5}$ 7.5 Hz for **14**). The equatorial/axial 'displacement' ratio was 2:5. The reaction of **2** with sodium azide did not yield a 5-amino derivative — the analogue of **9**. At present we are unable to give an unambiguous explanation for the observed differences in the reactivity of **1** and **2** with sodium azide. Taking into account the known influence of the orientation of the oxime hydroxyl group on the chemical shifts of adjacent protons [2,16,17] and the δ values for H-1 and H-3 in **11**, **12** and **13**, **14**, respectively (in **11** and **12** H-1 is deshielded and H-3 is shielded as compared with compounds **13** and **14**), we assume that the hydroxyimino group has the *Z* orientation in **11** and **12** and *E* in **13** and **14**.

The ^{1}H NMR data for **7**–**14** show, as was observed earlier [4,6,10,18,19], the influence of the configuration of the hydroxyimino group at C-2 on the values of $J_{3,4}$ and $J_{4,5}$. It was established that the values of these constants are ca. 10 Hz for α-D-*arabino* isomers and ca. 3 and 10 Hz for α-D-*ribo* isomers, with *Z* configuration of the 2-hydroxyimino group, respectively, and indicate indirectly the $^4C_1$ conformation of the sugar ring. The same applies to compounds **7**–**12**. On the other hand, in α anomers with *E* configuration of the 2-hydroxyimino group, these coupling constants change and indicate deformation of the carbohydrate ring from the typical $^4C_1$ conformation [4,6,18,20]. This is observed for compounds **13** and **14**. The reasons for this deformation seem to be an unfavorable, nonbonding steric interaction in a $^4C_1$ conformer between the 2-hydroxyimino group with the *E* orientation and the substituent at C-3.

1. Experimental

General methods.—Melting points are uncorrected. Optical rotations were recorded using a Hilger–Watt polarimeter for solutions in $CHCl_3$. TLC was performed on Merck Kieselgel 60 F-254 plates with: (*A*) 3:1 CCl_4–acetone; (*B*) 2:1 toluene–EtOAc; (*C*) 3:1 toluene–EtOAc; (*D*) 5:1 CCl_4–acetone. ^{1}H NMR spectra ($CDCl_3$, internal Me_4Si) were recorded with a Varian XL-100 (100 MHz) instrument. IR spectra were recorded for Nujol mulls with a Perkin–Elmer 257 spectrophotometer. Field desorption mass spectra (FD-MS) were recorded using an MAT 711 mass spectrometer. Column chromatography was performed on MN Kieselgel 60 (< 0.08 mm).

Methyl (ethyl 2,3,4-tri-O-acetyl-α-D-glucopyranosid)uronate (**3**).—A solution of **1** [10] (0.32 g, 0.96 mmol), MeCHO (0.16 mL, 3 mmol), and 1 M

HCl (1 mL) in MeCN (4 mL) was stirred for 24 h at room temperature, until the starting compound disappeared (TLC, solvent *A*). Then $NaBH_4$ (0.14 g, 4 mmol) was added in small portions. The resulting solution was stirred for 3 h at ~ 20°C, then neutralized with AcOH and concentrated. The residue was treated conventionally with Ac_2O–pyridine. Column chromatography (solvent *A*) of the product gave **3** (75%, syrup); $[\alpha]_D^{20}$ +94° (*c* 1.32); R_f 0.54 (solvent *A*); IR: ν 1745 (C=O), 1230 cm^{-1} (O–C); ^1H NMR: δ 1.23 (t, 3 H, *Me*CH_2), 2.07, 2.12, 2.18 (3 s, each 3 H, 3 × Ac), 3.70 (m, 5 H, CO_2Me and MeCH_2), 4.40 (d, 1 H, H-5), 4,59 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 5.20 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.23 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.60 (dd, 1 H, $J_{3,4}$ 10 Hz, H-3); FD-MS: *m/z* 362 (M^+).

Methyl 2-acetoxyimino-1,3,4-tri-O-*acetyl-2-deoxy*-D-arabino-*hexopyranuronate* (**6**), N-tert-*butoxycarbonyl*-O-(*methyl 2,3,4-tri*-O-*acetyl-α*-D-*gluco*- (**4**) *and* -*α*-D-*manno-pyranosyluronate*)-L-*serine methyl ester* (**5**). —A solution of **2** [10] (0.73 g, 1.4 mmol), MeCHO (0.24 mL, 4.3 mmol), and 1 M HCl (1.4 mL) in MeCN (6 mL) was stirred at ~ 20°C until the starting oxime disappeared (24 h, solvent *A*), and then the mixture was cooled to 0°C and treated with $NaBH_4$ (0.218 g, 5.7 mmol) in small portions. The resulting solution was stirred for 3 h at ~ 20°C, then neutralized with AcOH, and concentrated. The residue was treated with Ac_2O–pyridine, and the crude product was separated chromatographically (solvent *A*) to give, first, **6** (6%, syrup); $[\alpha]_D^{20}$ +116° (*c* 0.5); R_f 0.52 (solvent *A*); IR: ν 1780 (C=O in C=N–OAc), 1760 (C=O), 1645 (C=N), 1250 cm^{-1} (O–C); ^1H NMR: δ 2.07, 2.14, 2.18 (3 s, each 3 H, 3 × Ac), 3.80 (s, 3 H, OMe), 4.42 (d, 1 H, H-5), 5.60 (dd, 1 H, $J_{4,5}$ 8 Hz, H-4), 6.15 (d, 1 H, $J_{3,4}$ 7 Hz, H-3), 6.60 (s, 1 H, H-1); FD-MS: *m/z* 405 (M^+).

Eluted second was **4** (50%, syrup); $[\alpha]_D^{20}$ +106° (*c* 0.74); R_f 0.45 (solvent *A*); IR: ν 3260 (NH), 1730 (C=O), 1230 cm^{-1} (O–C); ^1H NMR: δ 1.47 (s, 9 H, NH*Boc*), 2.05 (s, 9 H, 3 × Ac), 3.77 (s, 6 H, 2 × CO_2Me), 4.0 (d, 2 H, Ser-H_β), 4.32 (d, 1 H, H-5), 4.60 (bs, 1 H, Ser-H_α), 4.87 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 5.15 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.18 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.45 (dd, 1 H, $J_{3,4}$ 10 Hz, H-3), 5.65 (bs, 1 H, Ser-NH); FD-MS: *m/z* 535 (M^+).

Eluted third was **5** (10%, syrup); $[\alpha]_D^{20}$ +15° (*c* 0.34); R_f 0.40 (solvent *A*); IR: ν 3260 (NH), 1745 (C=O), 1240 cm^{-1} (O–C); ^1H NMR: δ 1.46 (s, 9 H, NH*Boc*), 2.03, 2.08, 2.16 (3 s, each 3 H, 3 × Ac), 3.80 (s, 6 H, 2 × CO_2Me), 4.0 (s, 2 H, Ser-H_β), 4.12 (d, 1 H, H-5), 4.53 (m, 1 H, Ser-H_α), 4.77 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 5.12 (dd, 1 H, $J_{3,4}$ 10 Hz, H-3), 5.45 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.50 (bs, 1 H, Ser-N*H*), 5.82 (dd, 1 H, $J_{2,3}$ 3 Hz, H-2); FD-MS: *m/z* 535 (M^+).

Ethyl (5S)-4-O-*acetyl-5-amino-3-azido-2,3-dideoxy-2-(Z)-hydroxyimino-α*-D-threo-*pentopyranoside* (**9**) *and methyl (ethyl 4*-O-*acetyl-3-azido-2,3-dideoxy-2-(Z)-hydroxyimino-α*-D-arabino- (**7**) *and* -*α*-D-ribo-*hexopyranosid)uronate* (**8**).—A suspension of NaN_3 (0.78 g, 12 mmol) in a solution of **1** (1.05 g, 3 mmol) in EtOH (15 mL) was stirred and boiled under reflux. TLC (solvent *B*) after 1.5 h showed complete conversion of **1** into three products. The solution was filtered and concentrated, and the residue was extracted with ether. The extract was filtered, diluted with CH_2Cl_2 (100 mL), washed with water (3 × 15 mL), dried ($MgSO_4$), and concentrated. Column chromatography of the resulting syrup (solvent *C*) gave, first, **9** (5%, syrup); $[\alpha]_D^{20}$ +58° (*c* 0.3); R_f 0.50 (solvent *C*); IR: ν 3340 (OH, NH), 2120 (N_3), 1750 (C=O), 1235 cm^{-1} (O–C); ^1H NMR: δ 1.27 (t, 3 H, *Me*CH_2), 2.15 (s, 3 H, Ac), 3.82 (m, 2 H, MeCH_2), 4.25 (m, 1 H, H-5), 4.50 (d, 1 H, $J_{3,4}$ 10 Hz, H-3), 5.22 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4), 6.15 (s, 1 H, H-1); FD-MS: *m/z* 316 (M^+).

Eluted second was **7** (40%, syrup); $[\alpha]_D^{20}$ +52° (*c* 0.34); R_f 0.51 (solvent *C*); IR: ν 3260 (OH), 2090 (N_3), 1740 (C=O), 1225 cm^{-1} (O–C); ^1H NMR: δ 1.26 (t, 3 H, *Me*CH_2), 2.16 (s, 3 H, Ac), 3.80 (m, 5 H, CO_2Me and MeCH_2), 4.50 (d, 1 H, H-5), 4.52 (d, 1 H, $J_{3,4}$ 10 Hz, H-3), 5.20 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4), 6.15 (s, 1 H, H-1). Anal. Calcd for $C_{11}H_{16}N_4O_7$: C, 41.77; H, 5.10; N, 17.71. Found: C, 41.85; H, 5.14; N, 17.85.

Eluted third was **8** (20%, syrup); $[\alpha]_D^{20}$ +102° (*c* 1.48); R_f 0.42 (solvent *C*); IR: ν 3300 (OH), 2110 (N_3), 1740 (C=O), 1240 cm^{-1} (O–C); ^1H NMR: δ 1.25 (t, 3 H, *Me*CH_2), 2.12 (s, 3 H, Ac), 3.80 (s, 5 H, CO_2Me and MeCH_2), 4.80 (d, 1 H, H-5), 5.12 (m, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.66 (d, 1 H, $J_{3,4}$ 3.5 Hz, H-3), 6.00 (s, 1 H, H-1). Anal. Calcd for $C_{11}H_{16}N_4O_7$: C, 41.77; H, 5.10; N, 17.71. Found: C, 41.88; H, 5.19; N, 17.80.

Ethyl (5S)-5-acetamido-2-(Z)-acetoxyimino-4-O-*acetyl-3-azido-2,3-dideoxy-α*-D-threo-*pentopyranoside* (**10**).—Pyridine (0.5 mL), Ac_2O (0.5 mL), and a catalytic amount of 4-dimethylaminopyridine (DMAP) were added to a solution of **9** (0.25 g) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 3 h and then concentrated. A solution of the residue in $CHCl_3$ (15 mL) was washed with water (2 × 5 mL), dried ($MgSO_4$), and concentrated

in vacuo to give chromatographically pure **10** (70%, syrup); $[\alpha]_D^{20}$ +62° (*c* 0.2); R_f 0.75 (solvent *C*); IR: ν 3400 (NH), 2110 (N_3), 1750 (C=O), 1665 (amide C=O), 1240 cm^{-1} (O–C); ^1H NMR: δ 1.26 (t, 3 H, $MeCH_2$), 1.98, 2.10, 2.17 (3 s, each 3 H, 3 × Ac), 3.85 (m, 2 H, $MeCH_2$), 4.38 (dd, 1 H, H-5), 4.56 (d, 1 H, $J_{3,4}$ 10 Hz, H-3), 5.26 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4), 6.30 (s, 1 H, H-1), 7.90 (d, 1 H, NH, *J* 8 Hz). Anal. Calcd for $C_{13}H_{19}N_5O_7$: C, 43.70; H, 5.36; N, 19.60. Found: C, 43.90; H, 5.45; N, 19.75.

N-tert-*butoxycarbonyl*-O-*(methyl 4*-O-*acetyl*-3-*azido*-2,3-*dideoxy*-2-(Z)-*hydroxyimino*-α-D-arabino- (**11**) *and* -α-D-ribo-*hexopyranosyluronate)*-L-*serine methyl ester* (**12**), *and* N-tert-*butoxycarbonyl*-O-*(methyl 4*-O-*acetyl*-3-*azido*-2,3-*dideoxy*-2-(E)-*hydroxyimino*-α-D-arabino- (**13**), *and* -α-D-ribo-*hexopyranosyluronate)*-L-*serine methyl ester* (**14**).—A solution of **2** (0.685 g, 1.39 mmol) in EtOH (15 mL) was stirred and boiled under reflux with NaN_3 (0.35 g, 5.4 mmol). TLC (solvent *D*) after 1 h showed complete conversion of **2** into four products. The solution was filtered and concentrated, and the residue was treated with ether. The suspension was filtered again, diluted with CH_2Cl_2 (100 mL), washed with water (3 × 15 mL), dried ($MgSO_4$), and concentrated. Column chromatography of the crude residue (solvent *C*) gave, first, **11** (8%, syrup); $[\alpha]_D^{20}$ +60° (*c* 0.23); R_f 0.49 (solvent *C*); IR: ν 3260 (OH), 2100 (N_3), 1750 (C=O), 1225 cm^{-1} (O–C); ^1H NMR: δ 1.47 (s, 9 H, Ser-Boc), 2.15 (s, 3 H, Ac), 3.80 (s, 6 H, 2 × CO_2Me), 4.07 (d, 2 H, Ser-H_β), 4.40 (bs, 1 H, Ser-H_α), 4.47 (d, 1 H, $J_{3,4}$ 10 Hz, H-3), 4.50 (d, 1 H, H-5), 5.20 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.65 (bs, 1 H, Ser-NH), 6.06 (s, 1 H, H-1), 8.8 (bs, 1 H, OH). Anal. Calcd for $C_{18}H_{27}N_5O_{11}$: C, 44.17; H, 5.56; N, 14.31. Found: C, 44.10; H, 5.47; N, 14.45.

Eluted second was **12** (22%, syrup); $[\alpha]_D^{20}$ +84° (*c* 0.57); R_f 0.42 (solvent *C*); IR: ν 3200 (OH), 2100 (N_3), 1750 (C=O), 1230 cm^{-1} (O–C); ^1H NMR: δ 1.47 (s, 9 H, Ser-Boc), 2.12 (s, 3 H, Ac), 3.75 (s, 6 H, 2 × CO_2Me), 4.08 (bs, 2 H, Ser-H_β), 4.50 (bs, 1 H, Ser-H_α), 4.70 (d, 1 H, H-5), 4.73 (d, 1 H, $J_{3,4}$ 3 Hz, H-3), 5.12 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 5.57 (bs, 1 H, Ser-NH), 5.97 (s, 1 H, H-1). Anal. Calcd for $C_{18}H_{27}N_5O_{11}$: C, 44.17; H, 5.56; N, 14.31. Found: C, 44.05; H, 5.46; N, 14.42.

Eluted third was **13** (10%, syrup); $[\alpha]_D^{20}$ +46° (*c* 0.26); R_f 0.36 (solvent *C*); IR: ν 3250 (OH), 2090 (N_3), 1750 (C=O), 1225 cm^{-1} (O–C); ^1H NMR: δ 1.20 (s, 9 H, Ser-Boc), 2.13 (s, 3 H, Ac), 3.82 (s, 6 H, 2 × CO_2Me), 4.10 (bs, 2 H, Ser-H_β), 4.49 (d, 1 H, H-5), 4.50 (m, 1 H, Ser-H_α), 5.28 (s, 1 H, H-1), 5.18 (dd, 1 H, $J_{4,5}$ 7 Hz, H-4), 5.55 (bs, 1 H, Ser-NH), 5.65 (d, 1 H, $J_{3,4}$ 7 Hz, H-3), 9.07 (bs, 1 H, OH). Anal. Calcd for $C_{18}H_{27}N_5O_{11}$: C, 44.17; H, 5.56; N, 14.31. Found: C, 44.12; H, 5.40; N, 14.48.

Eluted fourth was **14** (22%, syrup); $[\alpha]_D^{20}$ +18° (*c* 0.55); R_f 0.31 (solvent *C*); IR: ν 3270 (OH), 2100 (N_3), 1755 (C=O), 1230 cm^{-1} (O–C); ^1H NMR: δ 1.20 (s, 9 H, Ser-Boc), 2.05 (s, 3 H, Ac), 3.77 (s, 6 H, 2 × CO_2Me), 4.07 (bs, 2 H, Ser-H_β), 4.23 (d, 1 H, H-5), 4.57 (bs, 1 H, Ser-H_α), 5.15 (m, 1 H, $J_{4,5}$ 7.5 Hz, H-4), 5.30 (s, 1 H, H-1), 5.55 (bs, 1 H, Ser-NH), 6.02 (d, 1 H, $J_{3,4}$ 5 Hz, H-3), 9.10 (bs, 1 H, OH). Anal. Calcd for $C_{18}H_{27}N_5O_{11}$: C, 44.17; H, 5.56; N, 14.31. Found: C, 44.03; H, 5.42; N, 14.41.

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