Carbohydrate Research, 196 (1990) 167–174
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

The synthesis, structure, and chemical transformation of methyl esters of *O*-(3,4-di-*O*-acetyl-2-deoxy-2-hydroxyimino-D-*erythro*-pentopyranosyl)-*N*-tosyl-L-serine, -L-threonine, and -L-tyrosine

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(Received March 30th, 1989; accepted for publication, July 5th, 1989)

The carbohydrate and peptide fragments of glycoproteins are often connected by α- or β-glycosidic linkages. Several methods have been developed[1] for the formation of such linkages, mostly β.

From 3,4,6-tri-*O*-acetyl-2-deoxy-2-nitroso-α-D-glucopyranosyl chloride have been synthesised *O*-glycosyl derivatives of L-serine, L-threonine, and L-tyrosine[2], and we now report analogous syntheses from 3,4-di-*O*-acetyl-2-deoxy-2-nitroso-β-D-arabinopyranosyl chloride (**1**).

The reaction of **1** for 48 h in *N,N*-dimethylformamide at ~20° severally with 1.4 equiv. of the methyl esters of *N*-tosyl-L-serine (**3**), -L-threonine (**4**), and -L-tyrosine (**5**) gave the corresponding 3,4-di-*O*-acetyl-2-deoxy-2-hydroxyimino-D-*erythro*-pentopyranosides **6**–**10**. The yield of the tyrosine glycoside **10** was reduced, probably due to cleavage of the *O*-glycosyl linkage during the isolation procedure, and this problem has been discussed in detail[2].

The 2-deoxy-2-hydroxyimino structure of **6**–**10** was indicated by the signals for H-1 (s) and H-3 (d) in the ^{1}H-n.m.r. spectra and the i.r. bands due to OH (3200 cm^{-1}) and C=N (1650 cm^{-1}) groups, as well as on the intensity of signals for two methyl groups corresponding to two acetyl groups.

The reaction of **1** with **3** and **4** gave ~1:1 mixtures of the α (**6** and **8**) and β anomers (**7** and **9**), but the reaction with **5** gave exclusively the β anomer (**10**).

The $^4C_1$ α-D-*erythro* structures of **6** and **8** and the $^1C_4$ β-D-*erythro* structures of **7**, **9**, and **10** were established on the basis of ^{1}H-n.m.r. data. The high and comparable δ values for the signals of H-1 for the α and β anomers indicated both protons to be equatorial; the small $\Delta\delta$ value (0.2 p.p.m.) for H-1α/H-1β is due to different conformations of the sugar ring. For the same conformation but different spatial orientation of the aglycon, the $\Delta\delta$ value should[3] be ~0.55 p.p.m. The $J_{4,5}$ values indicated H-4 to be axial in **6** and **8** ($J_{4,5e}$ ~3, $J_{4,5a}$ ~8 Hz) and equatorial in **7**, **9**, and **10** ($J_{4,5e}$ 1, $J_{4,5a}$ 3 Hz). Despite its axial orientation, H-3 in **7**, **9**, and **10** was

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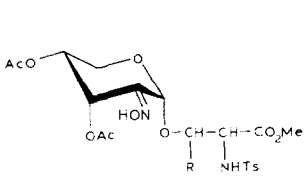
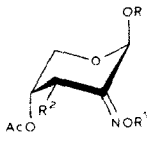
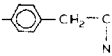


6 R = H
8 R = Me



7 R = $CH_2-CH-CO_2Me$, R^1 = H, R^2 = OAc
NHTs

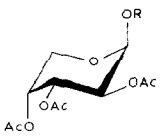
9 R = $CH-CH-CO_2Me$, R^1 = H, R^2 = OAc
CH_3 NHTs

10 R =  $CH_2-CH-CO_2Me$, R^1 = H, R^2 = OAc
NHTs

21 R = $CH_2-CH-CO_2Me$, R^1 = H, R^2 = N_3
NHTs

22 R = $CH-CH-CO_2Me$, R^1 = H, R^2 = N_3
CH_3 NHTs

23 R = $CH-CH-CO_2Me$, R^1 = Ac, R^2 = NHAc
CH_3 NHTs



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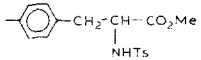
NHTs

14 R = $CH-CH-CO_2Me$
CH_3 NHTs

16 R = 
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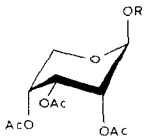

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NHTs

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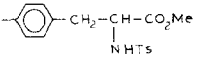
CH_3 NHTs

17 R = 
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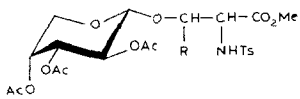

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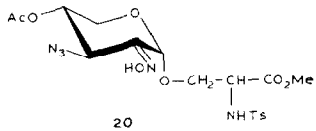
19 R = Me



20

more deshielded (~0.6 p.p.m.) than the equatorial H-3 in **6** and **8**, owing to the deshielding effect[4] of the axial substituents at C-2 and C-4. It is assumed that **6** and **8** are formed in the $^1C_4$ conformation. However, a strong dipole–dipole interaction[5] of the substituents at positions 1–3 results in a change to the $^4C_1$ conformation.

The known influence of the orientation of the oxime hydroxyl group on the chemical shifts in the ^{1}H-n.m.r. spectra[6–8] and the small $\Delta\delta$ value ratio (0.2 p.p.m.) for H-1α/H-1β indicate that the hydroxyimino group in the above α and β anomers has the *Z* configuration.

Deoximation of **6**, **7**, **9**, and **10** severally with acetaldehyde, borohydride reduction of the resulting ketone, and then acetylation gave the methyl esters of the corresponding *O*-(2,3,4-tri-*O*-acetyl-D-pentopyranosyl)-*N*-tosyl-L-amino acids (**11–17**). The β-D-*erythro* isomers **7**, **9**, and **10** gave the β-D-*arabino* derivatives **12**, **14**, and **16** ($^1C_4$, $J_{1,2} = J_{3,4} = 3$, $J_{2,3}$ 10 Hz) and the β-D-*ribo* derivatives **13**, **15**, and

TABLE I

^{1}H-N.M.R. DATA FOR **6–23** (δ IN p.p.m., J IN Hz)

Compound	*Sugar residue*													*Amino acid residue*					
	H-1	*H-2*	*H-3*	*H-4*	*H-5e*	*H-5a*	$\Delta\delta$ *H-5e/H-5a*	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5e}$	$J_{4,5a}$	J_{gem}	*OAc*	H_α	H_β	*NH*	$J_{CH\text{-}NH}$	*COOMe*	*NTs*
6	5.70s	—	5.00d	4.90dd	4.10–3.58m		—	—	—	3.5	3.0	8.0	—	1.90 (3 H) 2.00 (3 H)	4.10–3.58m		6.50d	6.0	3.45s	2.30 (3 H), 7.28 (2 H) 7.73 (2 H)
7	5.89s	—	5.58d	5.21dd	4.00dd	3.80dd	0.20	—	—	4.0	1.5	2.5	12	1.97 (6 H)	4.10m	3.73m	4.92d	8.0	3.45s	2.55 (3 H), 7.20 (2 H) 7.65 (2 H)
8	5.70s	—	4.98d	4.93dd	4.00–3.60m		—	—	—	3.5	4.0	8.0	—	1.90 (3 H) 2.03 (3 H)	4.18m	3.85m	5.60d	10.0	3.40s	2.30 (3 H), 7.23 (2 H) 7.68 (2 H)
9	5.95s	—	5.58d	5.18dd	3.93dd	3.70dd	0.23	—	—	4.0	1.5	3.0	14	1.95 (6 H)	4.23m	3.83m	5.88d	9.0	3.38s	2.28 (3 H), 7.20 (2 H) 7.63 (2 H)
10	6.60s	—	5.95d	5.33dd	3.88dd	3.64dd	0.24	—	—	4.0	1.5	3.0	14	2.06 (6 H)	4.27m	3.95m	—	—	3.35s	2.25 (3 H), 7.10 (2 H) 7.50 (2 H)
11	4.77d	4.72dd	5.45dd	4.85m	3.87dd	3.62dd	0.25	3.0	3.0	3.5	3.0	8.0	10	1.92 (6 H) 2.05 (3 H)	4.13m	3.66m	5.58d	8.0	3.45s	2.43 (3 H), 7.25 (2 H) 7.70 (2 H)
12	5.10d	5.15dd	5.15dd	4.95m	4.00dd	3.90dd	0.10	3.0	9.0	3.0	1.5	2.5	10	1.92 (3 H) 2.04 (6 H)	4.73m	3.68m	6.60d	7.0	3.55s	2.38 (3 H), 7.35 (2 H) 7.80 (2 H)
13	4.97d	4.82dd	5.20dd	4.70m	3.70dd	3.62dd	0.08	1.5	3.0	3.0	1.5	3.0	10	1.93 (6 H) 2.00 (3 H)	4.00m	3.70m	5.15d	7.0	3.45s	2.30 (3 H), 7.23 (2 H) 7.80 (2 H)
14	5.10d	5.15dd	5.15dd	4.90m	4.01dd	3.92dd	0.09	3.0	9.0	3.0	1.5	2.5	10	1.93 (3 H) 2.00 (6 H)	4.20m	3.60m	5.40d	9.0	3.43s	2.35 (3 H), 7.35 (2 H) 7.80 (2 H)
15	4.95d	4.80dd	5.18dd	4.75m	3.70dd	3.62dd	0.08	1.5	3.0	3.0	1.5	3.0	10	1.95 (9 H)	4.18m	3.88m	5.40d	8.0	3.38s	2.30 (3 H), 7.25 (2 H) 7.68 (2 H)
16	5.72d	5.65dd	5.65dd	5.20dd	3.97dd	3.85dd	0.12	3.0	9.0	3.0	1.5	3.0	10	2.00 (3 H) 2.15 (6 H)	4.13m	2.95m	5.10d	7.0	3.50s	2.40 (3 H), 7.30 (2 H) 7.68 (2 H)
17	5.52d	5.42dd	5.72dd	5.27dd	3.72dd	3.65dd	0.07	1.5	3.0	3.0	1.5	3.0	10	2.03 (6 H) 2.13 (3 H)	4.20m	3.03m	5.08d	8.0	3.45s	2.38 (3 H), 7.33 (2 H) 7.63 (2 H)
18	5.25d	5.20dd	5.15dd	5.05dd	4.05dd	3.82dd	0.23	9.0	9.0	2.5	1.5	2.5	12	1.95 (6 H) 2.05 (3 H)	4.38m	3.70m	6.53d	7.0	3.50s	2.35 (3 H), 7.33 (2 H) 7.80 (2 H)
19	5.22d	5.17dd	5.10dd	5.02dd	4.05dd	3.82dd	0.23	9.0	9.0	2.5	1.5	3.0	12	1.92 (6 H) 2.03 (3 H)	4.43m	3.85m	—	—	3.45s	2.33 (3 H), 7.30 (2 H) 7.78 (2 H)
20	5.82s	—	4.90d	5.15m	4.02dd	3.80dd	0.22	—	—	8.5	3.0	8.5	10	2.10 (3 H)	4.10–4.63m		—	—	3.48s	2.33 (3 H), 7.21 (2 H) 7.65 (2 H)
21	6.00s	—	4.64d	5.20m	3.96dd	3.17dd	0.19	—	—	3.0	1.5	2.5	10	2.01 (3 H)	4.23m	3.72m	—	—	3.58s	2.40 (3 H), 7.30 (2 H) 7.75 (2 H)
22	6.02s	—	4.67d	5.20m	4.05dd	3.85dd	0.20	—	—	3.0	1.5	2.5	10	2.10 (3 H)	4.25m	3.80m	6.50d	7.0	3.53s	2.43 (3 H), 7.38 (2 H) 7.83 (2 H)
23	6.00s	—	5.75d	5.22dd	3.95dd	3.75dd	0.20	—	—	3.0	1.5	3.0	10	2.00 (3 H) 2.05 (6 H)	4.38m	4.10m	6.00d	7.0	3.52s	2.43 (3 H), 7.40 (2 H) 7.85 (2 H)

17 ($^1C_4$, $J_{1,2}$ 1.5, $J_{2,3} = J_{3,4} = 3$ Hz) in the ratio 2:1 in an overall yield of ~60%. The $J_{1,2}$ values of 3 and 1.5 Hz correspond[9] to $J_{a,e}$ and $J_{e,e}$, respectively. Analogous transformations of the α-D-*erythro* isomer (**6**) gave only the α-D-*ribo* derivative **11** ($^4C_1$, $J_{1,2} = J_{2,3} = J_{3,4} = 3$ Hz), *i.e.*, the product of axial addition of the hydride ion to the carbonyl group as predicted[10]. In contrast, the reduction of the β-D-*erythro* ketones was not stereospecific; the addition occurred from the axial (→ **12**, **14**, and **16**) and equatorial (→ **13**, **15**, and **17**) sides.

The reaction of 2,3,4-tri-*O*-acetyl-β-D-arabinopyranosyl bromide (**2**) with **3** and **4** under Koenigs–Knorr conditions gave small yields of **12** and **14**; however, as predicted (participating group at C-2 and β configuration of **2**), the chief products were their α-*arabino* anomers (**18** and **19**, $^1C_4$, $J_{1,2} = J_{2,3} = 9$, $J_{3,4}$ 3 Hz).

The ^{1}H-n.m.r. data (Table I) show that, in the D-*ribo* series (**13**, **15**, and **17**), H-3 is the most deshielded proton in the sugar moiety, this being due to interaction[4] with the axial substituents at positions 1, 2, and 4. A comparison of the $[M]_D$ values of **6**–**17** shows that the new chiral center at C-2 adds to the total $[M]_D$ value of the β-D-*arabino* ($^1C_4$), β-D-*ribo* ($^1C_4$), and α-D-*ribo* ($^4C_1$) isomers approximately −400°, +200°, and −150°, respectively.

Compounds **6**, **7**, and **9** were also modified at C-3. Thus, on reaction of these compounds with sodium azide in boiling ethanol, AcO-3 was replaced by azide in an elimination–addition process[11] to give, respectively, **20** (α-D-*threo*, $^4C_1$, $J_{3,4} = J_{4,5e} = 9$ Hz), and **21** and **22** (β-D-*threo*, $^1C_4$, $J_{3,4} = J_{4,5a} = 3$ Hz). Contrary to earlier findings[12,13], this reaction was stereospecific, affording exclusively products with the azide group equatorial.

The azide group in **22** was reduced selectively with hydrogen over Pd/C and the hydroxyimine group remained intact. Acetylation of the product gave the 3-acetamido-2-acetoxyimino-β-D-*threo* derivative **23**, ($^1C_4$, $J_{3,4}$ 3 Hz).

EXPERIMENTAL

Melting points are uncorrected. Optical rotations were determined (Hilger–Watt instrument) for solutions in chloroform (*c* 0.5). ^{1}H-N.m.r. spectra ($CDCl_3$, internal Me_4Si) were recorded with a Tesla-BS 567A (100 MHz) spectrometer, i.r. spectra (Nujol mulls) with a Perkin–Elmer 257 spectrophotometer, and f.d.-mass spectra with a MAT 711 mass spectrometer. Column chromatography was performed on Kieselgel (<0.08 mm) and t.l.c. on silica gel G with *A*, carbon tetrachloride–ether (1:1); *B*, chloroform–ether (7:2); *C*, carbon tetrachloride–acetone (3:1); *D*, toluene–ethyl acetate (2:1); *E*, carbon tetrachloride–acetone (1:1).

Dimeric 3,4-di-*O*-acetyl-2-deoxy-2-nitroso-β-D-arabinopyranosyl chloride (**1**), m.p. 112–114°, $[\alpha]_D$ −206° (*c* 0.5, chloroform) (lit. [14] m.p. 126–128°, $[\alpha]_D$ −211°; lit.[15] m.p. 116–121°, $[\alpha]_D$ −203.2°) was prepared according to the literature procedure[14]. 2,3,4-Tri-*O*-acetyl-β-D-arabinopyranosyl bromide (**2**) had m.p. 138–140°, $[\alpha]_D$ −302° (*c* 0.5, chloroform); lit.[16,17] m.p. 137°, $[\alpha]_D^{20}$ −290.7° (chloroform).

N-Tosyl-L-serine methyl ester (**3**, m.p. 89–90°; lit.[18] m.p. 92–93°) and *N*-tosyl-L-threonine methyl ester (**4**, m.p. 99–101°; lit.[19] m.p. 100–101°) were prepared by the literature procedures[18,19]. The corresponding L-tyrosine derivative (**5**, m.p. 127–130°) was obtained as described[19] for **4**.

General procedure for the preparation of **6–10**. — The reaction of **1** (7 mmol) severally with **3–5** (10 mmol) in the molar ratio 1:1.4 was carried out in *N,N*-dimethylformamide (8 mL) until **1** disappeared (~48 h; t.l.c., solvent *A*). The mixture was diluted with dichloromethane (200 mL), washed with saturated aq. sodium hydrogencarbonate (3 × 20 mL) and water (3 × 15 mL), dried (Na_2SO_4), and concentrated *in vacuo*, and the residue was subjected to column chromatography.

O-*(3,4-Di-O-acetyl-2-deoxy-2-hydroxyimino-α- and -β-*D-erythro-*pentopyranosyl)*-N-*tosyl*-L-*serine methyl ester* (**6** *and* **7**). — Chromatography (solvent *A*) of the crude product from the reaction of **1** with **3** (3.5 g) gave, first, **6** (syrup, 30%), $[\alpha]_D^{20}$ +92°, R_F 0.32 (solvent *A*); ν_{max} 3300 (OH, NH), 1748 (ester CO), and 1600 cm^{-1} (oxime CN).

Anal. Calc. for $C_{20}H_{26}N_2O_{11}S$: C, 47.80; H, 5.22; N, 5.58. Found: C, 47.50; H, 5.20; N, 5.38.

Eluted second was **7** (syrup, 31%), $[\alpha]_D^{20}$ −82°, R_F 0.25; ν_{max} 3250 (OH, NH), 1740 (ester CO), and 1610 cm^{-1} (oxime CN).

Anal. Found: C, 47.55; H, 5.18; N, 5.42.

O-*(3,4-Di-O-acetyl-2-deoxy-2-hydroxyimino-α- and -β-*D-erythro-*pentopyranosyl)*-N-*tosyl*-L-*threonine methyl ester* (**8** *and* **9**). — Chromatography (solvent *A*) of the crude product of the reaction of **1** with **4** (4.1 g) gave, first, **8** (syrup, 28%), $[\alpha]_D^{20}$ +40°, R_F 0.33 (solvent *A*); ν_{max} 3300 (OH, NH), 1740 (ester CO), and 1610 cm^{-1} (oxime CN).

Anal. Calc. for $C_{21}H_{28}N_2O_{11}S$: C, 48.83; H, 5.46; N, 5.42. Found: C, 48.50; H, 5.30; N, 5.35.

Eluted second was **9** (syrup, 33%), $[\alpha]_D^{20}$ −86°, R_F 0.25; ν_{max} 3220 (OH, NH), 1735 (ester CO), and 1600 cm^{-1} (oxime CN).

Anal. Found: C, 48.75; H, 5.40; N, 5.37.

O-*(3,4-Di-O-acetyl-2-deoxy-2-hydroxyimino-β-*D-erythro-*pentopyranosyl)*-N-*tosyl*-L-*tyrosine methyl ester* (**10**). — Column chromatograpy (solvent *B* then solvent *C*) of the mixture obtained by the reaction of **1** with **5** gave, first, **10** (syrup, 35%), $[\alpha]_D^{20}$ −42°, R_F 0.20 (solvent *C*); ν_{max} 3310 (OH, NH), 1745 (ester CO), and 1620 cm^{-1} (oxime CN).

Anal. Calc. for $C_{26}H_{30}N_2O_{11}S$: C, 53.97; H, 5.23; N, 4.84. Found: C, 53.99; H, 5.10; N, 4.70.

Eluted second was a syrupy product (10%) that had $[\alpha]_D^{20}$ +95°, R_F 0.14.

General procedure for transformation of the hydroxyimino derivatives (**6**, **7**, **9**, *and* **10**) *into 2,3,4-tri-*O-*acetyl-*D-*pentopyranosides* (**11–17**). — A solution of **6**, **7**, **9**, or **10** (3 mmol), acetaldehyde (9 mmol), and M hydrochloric acid (3 mL) in acetonitrile (15 mL) was stirred at 20° until the oxime disappeared (95 h for **6** and

7; or 45 h for **9** and **10**; t.l.c., solvent *C* or *D*), then cooled to 0°, and treated with sodium borohydride (15 mmol) in small portions. The mixture was stirred for 3 h at ~20°, cooled to 0°, neutralized with acetic acid, and concentrated. The residue was treated conventionally with acetic anhydride–pyridine. Column chromatography (solvent *D*) of the product gave **11–17**.

N-*Tosyl*-O-*(2,3,4-tri*-O-*acetyl-α*-D-*ribopyranosyl)*-L-serine methyl ester (**11**). — Prepared from **6**, **11** (syrup, 55%) had $[\alpha]_D^{20}$ +62°, R_F 0.38 (solvent *C*); ν_{max} 3200 (NH) and 1735 cm^{-1} (ester CO). F.d.-mass spectrum: *m/z* 531 (M^+].

Anal. Calc. for $C_{22}H_{29}NO_{12}S$: C, 49.71; H, 5.50; N, 2.64. Found: C, 49.79; H, 5.55; N, 2.68.

N-*Tosyl*-O-*(2,3,4-tri*-O-*acetyl-β*-D-*arabinopyranosyl and -β*-D-*ribopyranosyl)*-L-*serine methyl ester* (**12** *and* **13**). — Prepared from **7**, **12** (syrup, 25%) had $[\alpha]_D^{20}$ −158°, R_F 0.34 (solvent *D*); ν_{max} 3200 (NH) and 1740 cm^{-1} (ester CO). F.d.-mass spectrum: *m/z* 531 [M^+].

Anal. Calc. for $C_{22}H_{29}NO_{12}S$: C, 49.71; H, 5.50; N, 2.64. Found: C, 49.80; H, 5.52; N, 2.70.

Eluted second was **13** (syrup, 35%), $[\alpha]_D^{20}$ −25°, R_F 0.24; ν_{max} 3180 (NH) and 1735 cm^{-1} (ester CO). F.d.-mass spectrum: *m/z* 531 [M^+].

Anal. Found: C, 49.70; H, 5.52; N, 2.70.

N-*Tosyl*-O-*(2,3,4-tri*-O-*acetyl-β*-D-*arabinopyranosyl and -β*-D-*ribopyranosyl)*-L-*threonine methyl ester* (**14** *and* **15**). — Prepared from **9**, **14** (syrup, 48%) had $[\alpha]_D^{20}$ −150°, R_F 0.40 (solvent *D*); ν_{max} 3200 (NH) and 1740 cm^{-1} (ester CO). F.d.-mass spectrum: *m/z* 545 [M^+].

Anal. Calc. for $C_{23}H_{31}NO_{12}S$: C, 50.63; H, 5.73; N, 2.57. Found: C, 50.68; H, 5.75; N, 2.60.

Eluted second was **15** (syrup, 22%), $[\alpha]_D^{20}$ −46°, R_F 0.25 (solvent *D*); ν_{max} 3200 (NH) and 1735 cm^{-1} (ester CO). F.d.-mass spectrum: *m/z* 545 [M^+].

Anal. Found: C, 50.60; H, 5.70; N, 2.60.

N-*Tosyl*-O-*(2,3,4-tri*-O-*acetyl-β*-D-*arabinopyranosyl and -β*-D-*ribopyranosyl)*-L-*tyrosine methyl ester* (**16** *and* **17**). — Prepared from **10**, **16** (syrup, 32%) had $[\alpha]_D^{20}$ −117°, R_F 0.47 (solvent *D*); ν_{max} 3200 (NH) and 1730 cm^{-1} (ester CO). F.d.-mass spectrum: *m/z* 607 [M^+].

Anal. Calc. for $C_{28}H_{33}NO_{12}S$: C, 55.34; H, 5.47; N, 2.31. Found: C, 55.40; H, 5.52; N, 2.37.

Eluted second was **17** (syrup, 15%), $[\alpha]_D^{20}$ −6°, R_F 0.38 (solvent *D*); ν_{max} 3220 (NH) and 1745 cm^{-1} (ester CO). F.d.-mass spectrum: *m/z* 607 [M^+].

Anal. Found: C, 55.42; H, 5.50; N, 2.50.

Reaction of 2,3,4-tri-O-*acetyl-β*-D-*arabinopyranosyl bromide* (**2**) *with* **3** *and* **4**. — To a solution of **2** (3 mmol, 1.017 g) or **3** (3.3 mmol, 0.224 g) in benzene–nitromethane (1:1) (34 mL) was added $Hg(CN)_2$ (0.760 g, 3 mmol), and the mixture was stirred at room temperature until **2** had reacted (24 h; t.l.c., solvent *C*). The mixture was filtered, treated with ether, filtered, diluted with chloroform (200 mL), washed with water, dried ($MgSO_4$), and concentrated. Column chromatography

(solvent *D*) of the crude product gave, first, **12** (32%). Eluted second was *N*-tosyl-*O*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-L-serine methyl ester (**18**; syrup, 43%), $[\alpha]_D^{20}$ −22°, R_F 0.28 (solvent *D*); ν_{max} 3250 (NH) and 1740 cm^{-1} (ester CO). F.d.-mass spectrum: *m/z* 531 [M^+].

Anal. Calc. for $C_{22}H_{29}NO_{12}S$: C, 49.71; H, 5.50; N, 2.64. Found: C, 49.80; H, 5.55; N, 2.70.

Likewise, the reaction of **2** with **4** gave **14** (27%) and *N*-tosyl-*O*-(2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl)-L-threonine methyl ester (**19**; syrup, 46%), $[\alpha]_D^{20}$ −7°, R_F 0.35 (solvent *D*); ν_{max} 3220 (NH) and 1730 cm^{-1} (ester CO). F.d.-mass spectrum: *m/z* 545 [M^+].

Anal. Calc. for $C_{23}H_{31}NO_{12}S$: C, 50.63; H, 5.73; N, 2.57. Found: C, 50.70; H, 5.75; N, 2.60.

O-*(4-O-Acetyl-3-azido-2,3-dideoxy-2-hydroxyimino-α-*D-threo-*pentopyranosyl)*-N-*tosyl-*L-*serine methyl ester* (**20**). — A solution of **6** (0.31 g, 0.6 mmol) in ethanol (30 mL) was stirred and boiled under reflux with sodium azide (0.156 g, 2.4 mmol). T.l.c. (solvent *A*) after 2 h showed the complete conversion of **6** into one product. The solution was filtered and concentrated. Column chromatography (solvent *A*) of the product gave **20** (syrup, 75%), $[\alpha]_D^{20}$ +71°, R_F 0.68 (solvent *A*); ν_{max} 3300 (OH, NH), 2100 (N_3), and 1740 cm^{-1} (ester CO). F.d.-mass spectrum: *m/z* 486 [$M^+ + 1$].

Anal. Calc. for $C_{18}H_{23}N_5O_9S$: C, 44.53; H, 4.77; N, 14.43. Found: C, 44.60; H, 4.81; N, 14.48.

Similar treatment of **7** gave O-*(4-O-acetyl-3-azido-2,3-dideoxy-2-hydroxyimino-β-*D-*erythro*-pentopyranosyl)-*N*-tosyl-L-serine methyl ester (**21**; syrup, 60%), $[\alpha]_D^{20}$ −41°, R_F 0.63 (solvent *A*); ν_{max} 3280 (OH, NH), 2120 (N_3), and 1730 cm^{-1} (ester CO). F.d.-mass spectrum: *m/z* 486 [$M^+ + 1$).

Anal. Calc. for $C_{18}H_{23}N_5O_9S$: C, 44.53; H, 4.77; N, 14.43. Found: C, 44.60; H, 4.80; N, 14.45.

Likewise, **9** gave *O*-(4-*O*-acetyl-3-azido-2,3-dideoxy-2-hydroxyimino-β-D-*erythro*-pentopyranosyl)-*N*-tosyl-L-threonine methyl ester (**22**; syrup, 66%), $[\alpha]_D^{20}$ −53°, R_F 0.78 (solvent *A*); ν_{max} 3290 (OH, NH), 2120 (N_3), and 1740 cm^{-1} (ester CO). F.d.-mass spectrum: *m/z* 499 [M^+].

Anal. Calc. for $C_{19}H_{25}N_5O_9S$: C, 45.68; H, 5.05; N, 14.02. Found: C, 45.75; H, 5.10; N, 14.10.

O-*(3-Acetamido-2-acetoxyimino-4-*O-*acetyl-2,3-dideoxy-β-*D-erythro-*pentopyranosyl)*-N-*tosyl-*L-threonine methyl ester* (**23**). — A solution of **22** (0.3 g, 0.6 mmol) in ethanol (15 mL) was hydrogenated in the presence of 5% Pd/C (0.2 g) for 3 h at 20°. The catalyst was removed, the filtrate was concentrated, and the residue was treatment conventionally with pyridine–acetic anhydride. Column chromatography (solvent *E*) of the product gave **23** (syrup, 75%), $[\alpha]_D^{20}$ −129°, R_F 0.56 (solvent *E*); ν_{max} 3250 (NH), 1750 (ester CO), and 1660 cm^{-1} (amide CO). F.d.-mass spectrum: *m/z* 558 [$M^+ + 1$].

Anal. Calc. for $C_{23}H_{31}N_9O_{11}S$: C, 49.54; H, 5.60; N, 7.54. Found: C, 49.60; H, 5.65; N, 7.60.

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