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TARTRALDEHYDES III[1]. SYNTHESIS OF N-BENZOYL-L-RISTOSAMINE AND -L-ACOSAMINE

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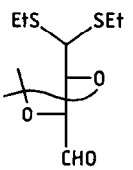
Abstract: The title compounds have been synthesized from the (2R,3S)--tartraldehyde mercaptal **4** in seven steps with 21 % overall yield.

Recently we have prepared isopropylidene tartraldehyde mercaptals **1** and **2**[1,2] (Scheme 1). These compounds proved to be versatile starting materials in the synthesis of several deoxyhexoses, such as daunosamine[2], diginose and sarmentose[1].



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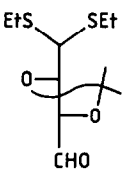

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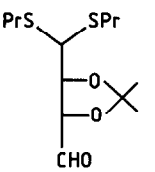
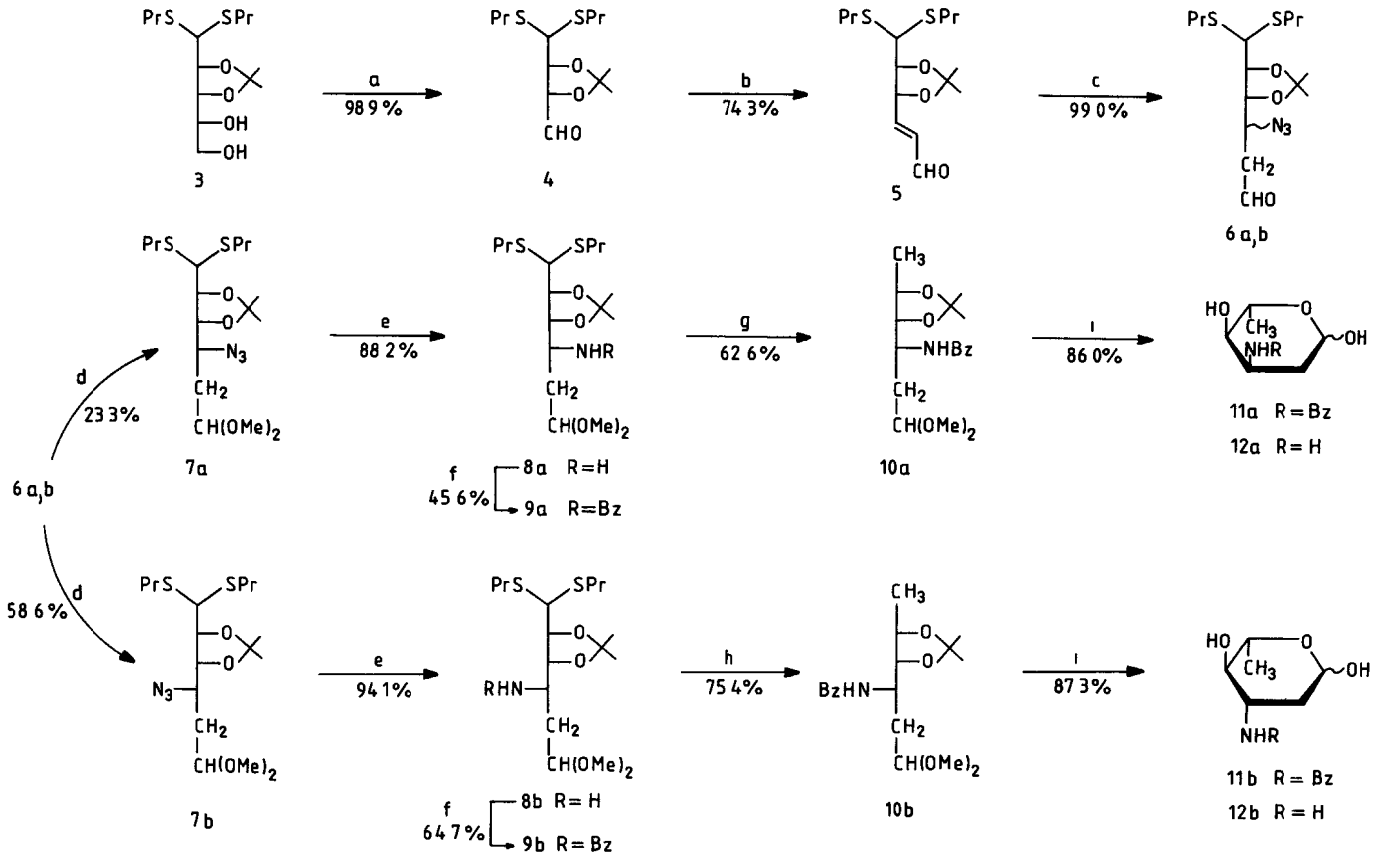


4

SCHEME 1

Continuing that work we have targeted the synthesis of two biologically important 3-amino-2,3,6-trideoxy-hexoses, L-ristosamine (**12a**) and L-acosamine (**12b**), sugar constituents of antibiotics. L-Ristosamine is a component of actinoidins[4,5]. In the past few years numerous syntheses of **12a** and **12b** have been published[5,6].

In our new synthetic route the (2R,3S) diastereomeric tartraldehyde mercaptal **4** served as starting compound. **4** Could be prepared from the 2,3-O-isopropylidene-D-ribose mercaptal[7] **3** by glycol-cleaving reaction with lead-



(a) $Pb(OAc)_4$/PhH, rt, 10 min,
(b) $Ph_3PCHCHO$/PhH, reflux, 1 h,
(c) NaN_3/AcOH, rt, 10-12 h,
(d) MeOH, TsOH (cat)/DMP, rt, 1 h,
(e) $LiAlH_4/Et_2O$, rt, 30 min,
(f) BzCl/Py, 0 °C, 2 h,
(g) Ra-Ni/MeOH, 60 °C, 1 h,
(h) Ra-Ni/EtOH, reflux, 1 h,
(i) AcOH/H_2O, 60 °C, 1 h

SCHEME 2

(IV)acetate (scheme 2) and it was characterized in the form of its 4-nitrophenylhydrazone.

The synthesis of **11a** and **11b** was carried out in a similar way we have reported for daunosamine[2]. The carbon skeleton of **11a** and **11b** was built up by chain elongation of **4** with formylmethylenetriphenylphosphorane[8] obtaining trans-alkenal **5** exclusively. Conjugate addition of hydrazoic acid to the double bond of **5** led to the stereoselective formation of **6a,b**. The ratio of diastereomers was 2:5 in favour of the 3,4-trans product. Aldehydo functions of **6a,b** were protected in the form of dimethyl acetals using methanol and acid catalyst in the presence of 2,2-dimethoxypropane to avoid methanolysis of the dioxolane ring. **7a** and **7b** could be separated by column chromatography. Amino compounds **8a** and **8b** were obtained from the latter upon reduction of the azido functions with lithium tetrahydridoaluminate. Reductive desulfurization of the corresponding N-benzoates **9a** and **9b** with Raney nickel provided the terminal deoxy functions of the target compounds to give **10a** and **10b**, respectively. In the last step the acetal type protective groups were removed by acid hydrolysis obtaining N-benzoyl-L-ristosamine **11a** and -L-acosamine **11b**. The overall yield for the seven-step sequence **4** ⟶ **11a** + **11b** was 21 %.

Using this widely applicable method we have synthesized six diastereomers of the possible eight of 3-amino-2,3,6-trideoxyhexoses and four 2,6-dideoxyhexose-3-O-methyl ethers. The versatility of tartraldehyde mercaptals can be exploited in another ways: e.g. another functional groups can be introduced into the 3-position of 2,6-dideoxyhexoses or the carbon skeleton can be extended after demercaptalization giving rise to dichiral, long-chain synthetic building blocks. Investigations in this field are under way in our laboratory.

EXPERIMENTAL

General methods: Organic extracts were dried with anhydrous magnesium sulfate. Solutions were concentrated at 40°C (bath) at ca 17 mmHg. Adsorption chromatography was carried out using Kieselgel 60. For TLC, precoated aluminiumbacked plate (Kieselgel 60 F_{254}, Merck) were used. Melting points were determined on a Kofler melting point apparatus and were uncorrected. IR spectra (KBr discs) were recorded on a Perkin-Elmer 283 B spectrophotometer. Mass spectrometry was performed using a VG-7035 GC/MS/D5 instrument (70 eV). NMR spectra were obtained by using a Bruker WP-200 SY spectrometer. Specific rotations were measured at room temperature on a Perkin-Elmer 141 MC polarimeter.

2,3-O-Isopropylidene-D-*erythro*-tetrodialdose 1,1-di(n-propyl)dithioacetal (**4**): To a well stirred solution of 2,3-O-isopropylidene-D-ribose di-(n-propyl)mercaptal[7] (**3**) (5.06 g, 15.6 mmol) in dry benzene (155 ml) lead-(IV)acetate (7.60 g, 17.1 mmol) was added. After 10 minutes the reaction mixture was filtered through a Celite pad, washed with benzene(2x50ml). The combined aqueous phase was reextracted with benzene (2x50 ml). The organic layers were washed with $NaHCO_3$ solution (30 ml) again. The dried benzene extracts were evaporated to give crude **4** (4.51 g, 98.9 %) as a light yellow syrup , which was used for the next step without further purification. **4** was characterized as its p-nitrophenylhydrazone: m.p. 101°C. $[\alpha]_D$ -70.5 (c 1.63, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.90-1.05 (m, 6H, CH_2CH_3), 1.44 and 1.59 (2s, 6H, $C(CH_3)_2$), 1.40-1.70 (m, 4H, $CH_2CH_2CH_3$), 2.58-2.81 (m, 4H, SCH_2), 3.81 (d, 1H, H-1), 4.58 (dd, 1H, H-2), 4.89 (dd, 1H, H-3), 6.99-7.10 and 8.12-8.22 (m, 4H, ArCH), 7.33 (dd, 1H, H-4), 7.95 (br, 1H, NH) ppm. Anal. Calcd. for $C_{19}H_{29}N_3O_4S_2$: C, 53.37, H, 6.84, N, 9.83. Found: C, 53.51, H, 7.01, N,9.65.

4,5-Dideoxy-2,3-O-isopropylidene-D-*erythro*-hex-4E-eno-dialdose 1,1-di-(n-propyl)dithioacetal (**5**):A dry benzene (145 ml) solution of **4** (3.89 g, 13.3 mmol) and formylmethylenetriphenylphosporane[8] (4.25 g, 14.0 mmol) was heated at reflux for 50-60 minutes. After evaporation of the solvent in vacuum the residue was purified by column chromatography using hexanes--EtOAc (10:1) mixture as eluent, to yield **5** (3.15 g, 74.3 %) as an oil. $[\alpha]_D$ +9.0 (c 0.86, $CHCl_3$).IR: 1685 cm^{-1} (CHO). MS m/e: 318 (M^+). ^{1}H NMR ($CDCl_3$): δ 1.00 (t, 6H, CH_2CH_3), 1.43 and 1.57 (2s, 6H, $C(CH_3)_2$), 1.50-1.70 (m, 4H, $CH_2CH_2CH_3$), 2.50-2.85 (m, 4H, SCH_2), 3.63 (d, 1H,$J_{1,2}$= 9.5 Hz,H-1), 4.39 (dd, 1H, $J_{2,3}$= 6.5 Hz, H-2), 4.91 (ddd, 1H, $J_{3,4}$= 5.5 Hz, $J_{3,5}$= 1.5 Hz, H-3), 6.42 (ddd, 1H , $J_{4,5}$= 15.5 Hz, $J_{5,6}$= 8 Hz, H-5) 7.08 (dd, 1H, H-4), 9.63 (d, 1H, CHO) ppm. Anal. Calcd. for $C_{15}H_{26}O_3S_2$: C, 56.57, H, 8.23. Found: C, 56.53, H, 7.95.

4-Azido-4,5-dideoxy-2,3-O-isopropylidene-L-*lyxo*- and D-*ribo* hexodialdose 1,1-di(n-propyl) dithioacetal (**6a,b**): Sodium azide (5.61 g, 86 mmol) was added to a solution of **5** (2.749 g, 8.6 mmol) in acetic acid (25 ml) and the thick suspension was stirred overnight at room temperature. The reaction mixture was taken up in dichloromethane (300 ml) and washed with saturated $NaHCO_3$ solution (2 x 80 ml). The dried organic phase was evaporated to give **6a,b** (3.090 g, 99.0 %) as an oil, which was utilized for the next step without further purification. IR: 2100 cm^{-1}($-N_3$), 1725 and 1690 cm^{-1}(CHO). MS m/e: 319 (M^+-N_3), 243 ($M^+-HN_3-SC_3H_7$). ^{1}H NMR ($CDCl_3$): δ 0.94-1.10 (m, 6H, CH_2CH_3), 1.37, 1.58 and 1.35, 1.49 (each 2s, 6H, $C(CH_3)_2$), 1.50-1.80 (m, 4H, $CH_2CH_2CH_3$), 2.50-2.85 (m, 4H, SCH_2), 2.60-3.15 (m, 2H, H-5), 3.90-4.65 (m, 4H, H-1, H-2, H-3, H-4), 9.87 (s, 1H, CHO) ppm.

4-Azido-4,5-dideoxy-2,3-O-isopropylidene-D-*ribo*-hexodialdose 6,6-dimethyl acetal 1,1-di(n-propyl) dithioacetal (**7a**) and 4-azido-4,5-dideoxy-2,3-O-isopropylidene-L-*lyxo*-hexodialdose 6,6-dimethyl acetal 1,1-di-(n-propyl) dithioacetal (**7b**): To a stirred solution of **6a,b** (2.774 g, 7.7 mmol) in 2.2-dimethoxypropane (10.0 ml) dry methanol (1.30 ml) and a catalytic amount of p-toluenesulfonic acid monohydrate was added. After 1 hour the reaction mixture was partitioned between dichloromethane (350 ml) and saturated $NaHCO_3$ solution (50 ml). The organic layer was concentrated and the two diastereoisomers were separated using column chromatography, eluting with hexanes-Et_2O-EtOAc (40:2:1) to yield pure **7a** (730 mg, 23.3%); $[\alpha]_D$ -5.6 (c 0.66, $CHCl_3$). IR: 2095 cm^{-1} ($-N_3$), ^1H NMR ($CDCl_3$): δ 1.02 (t, 6H, CH_2CH_3), 1.36 and 1.50 (2s, 6H, $C(CH_3)_2$), 1.55-1.76 (m, 4H, $CH_2CH_2CH_3$), 1.77-2.22 (m, 2H, H-5), 2.56-2.85 (m, 4H, SCH_2), 3.37 and 3.39 (2s, 6H, OCH_3), 3.89-4.03 (m, 1H, H-4), 4.04 (d, 1H, H-1), 4.10-4.45 (m, 2H, H-2, H-3), 4.60 (dd, 1H, H-6) ppm. Anal. Calcd. for $C_{17}H_{33}N_3O_4S_2$: C, 50.09, H, 8.16, N, 10.31. Found: C, 50.02, H, 8.02, N, 10.33; and

7b: (1.834 g, 58.6 %); $[\alpha]_D$ +84.2 (c 0.77, $CHCl_3$), IR: 2100 cm^{-1} ($-N_3$), ^1H NMR ($CDCl_3$): δ 1.02 (t, 6H, CH_2CH_3), 1.38 and 1.59 (2s, 6H, $C(CH_3)_2$), 1.50-1.78 (m, 4H, $CH_2CH_2CH_3$), 1.84-2.24 (m, 2H, H-5), 2.53-2.93 (m, 4H, SCH_2), 3.37 and 3.39 (2s, 6H, OCH_3), 3.83-3.95 (m, 1H, H-4), 4.05-4.30 (m, 3H, H-1, H-2, H-3), 4.55 (dd, 1H, H-6) ppm. Anal. Calcd. for $C_{17}H_{33}N_3O_4S_2$: C, 50.09, H, 8.16, N, 10.31. Found: C, 50.28, H, 8.18, N, 10.12.

4-Amino-4,5-dideoxy-2,3-O-isopropylidene-D-*ribo*-hexodialdose 6,6-dimethyl acetal 1,1-di(n-propyl) dithioacetal (**8a**): To a solution of **7a** (688 mg, 1.69 mmol) in dry ether (35 ml) lithium aluminium hydride (320 mg, 8.43 mmol) was added, and the mixture was stirred at room temperature for half an hour. After usual work up (EtOAc, 5 % NaOH solution) the crude product was purified by column chromatography, with hexanes-acetone (8:2) mixture as eluent resulted **8a** (568 mg, 88.2 %). $[\alpha]_D$ -22.6 (c 0.71, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.01 (t, 6H, CH_2CH_3), 1.34 and 1.48 (2s, 6H, $C(CH_3)_2$), 1.49-1.76 (m, 7H, $CH_2CH_2CH_3$, NH_2, H-5), 2.02-2.18 (m, 1H, H-5′), 2.53-2.83 (m, 4H, SCH_2), 3.35 and 3.36 (2s, 6H, OCH_3), 3.28-3.42 (m, 1H, H-4), 3.90-4.42 (m, 3H, H-1, H-2, H-3), 4.62 (dd, 1H, H-6) ppm. Anal. Calcd. for $C_{17}H_{35}NO_4S_2$: C, 53.51, H, 9.25, N, 3.67. Found: C, 53.25, H, 9.18, N, 3.62.

4-Amino-4,5-dideoxy-2,3-O-isopropylidene-L-*lyxo*-hexodialdose 6,6-dimethyl acetal 1,1-di(n-propyl) dithioacetal (**8b**): Following the same procedure employed for the preparation of **8a**, **7b** (1.700 g, 4.2 mmol) was reduced to furnish the amine which after column chromatography (hexanes-acetone, 8:2) afforded pure **8b** (1.497 g, 94.1 %).$[\alpha]_D$ -41.9 (c 0.70, $CHCl_3$). MS m/e: 382 (M^+ +1), 306 (M^+ $-SC_3H_7$). ^1H NMR: ($CDCl_3$): δ 0.93-1.07 (2t, 6H, CH_2CH_3), 1.40-1.52 (br, 2H, NH_2), 1.38 and 1.54 (2s, 6H, $C(CH_3)_2$), 1.55-

1.76 (m, 6H, $CH_2C\underline{H}_2CH_3$, H-5), 2.56-2.87 (m, 4H, SCH_2), 3.34 and 3.35 (2s, 6H, OCH_3), 3.27-3.49 (m, 1H, H-4), 3.95-4.40 (m, 3H, H-1, H-2, H-3), 4.59 (dd, 1H, H-6) ppm. Anal. Calcd. for $C_{17}H_{35}NO_4S_2$: C, 53.51, H, 9.25, N, 3.67. Found: C, 53.89, H, 9.12, N, 3.81.

4-Benzamido-4,5-dideoxy-2,3-O-isopropylidene-D-*ribo*-hexodialdose 6,6-dimethyl acetal 1,1-di(n-propyl) dithioacetal (**9a**): Compound **8a** (450 mg, 1.18 mmol) was acylated with benzoyl chloride (182 mg, 1.3 mmol) in pyridine (3.0 ml) for 2 hours at 0 °C. After usual work up and adsorption chromatography (hexanes-EtOAc, 85:15) pure **9a** (261 mg, 45.6 %) was obtained. M.p. 90-92 °C. $[\alpha]_D$ -6.5 (c 0.72, $CHCl_3$). IR:1639 cm^{-1} (amide-I), 1538 cm^{-1} (amide-II). MS m/e: 470 (M^+-CH_3), 410 ($M^+-SC_3H_7$). ^{1}H NMR ($CDCl_3$): δ 0.85-1.09 (2t, 6H, $CH_2C\underline{H}_3$), 1.38 and 1.55 (2s, 6H, $C(CH_3)_2$), 1.43-1.73 (m, 4H, $CH_2C\underline{H}_2CH_3$), 1.73-2.19 (m, 2H, H-5), 2.52-2.84 (m, 4H, SCH_2), 3.31 and 3.44 (2s, 6H, OCH_3), 4.15-4.93 (m, 5H, H-1, H-2, H-3, H-4, H-6), 6.64 (d, 1H, NH), 7.35-7.86 (m, 5H, ArCH) ppm. Anal. Calcd. for $C_{24}H_{39}NO_5S_2$:C, 59.35, H, 8.09, N, 2.88. Found: C, 59.78, H, 7.96, N, 2.85.

4-Benzamido-4,5-dideoxy-2,3-O-isopropylidene-L-*lyxo*-hexodialdose 6,6-dimethyl acetal 1,1-di(n-propyl) dithioacetal (**9b**): **8b** (1.094 g, 2.9 mmole) was converted to **9b** (900 mg, 64.7 %) in the same way as described for **9a**. $[\alpha]_D$ +63.3 (c 0.71, $CHCl_3$). IR: 1662 cm^{-1}(amide-I), 1508 cm^{-1} (amide-II). ^{1}H NMR ($CDCl_3$): δ 0.78 and 1.06 (2t, 6H, $CH_2C\underline{H}_3$), 1.43 and 1.56 (2s, 6H, $C(CH_3)_2$), 1.21-1.84 (m, 4H, $CH_2C\underline{H}_2CH_3$), 1.88-1.99 (m, 2H, H-5), 2.40-3.08 (m, 4H, SCH_2), 3.30 and 3.39 (2s, 6H, OCH_3), 4.01 (d, 1H, H-1), 4.06-4.88 (m, 4H, H-2, H-3, H-4, H-6), 6.53 (d, 1H, NH), 7.35-7.82 (m, 5H, ArCH) ppm. Anal. Calcd. for $C_{24}H_{39}NO_5S_2$: C, 59.35, H, 8.09, N, 2.88. Found: C, 59.71, H, 8.07, N, 2.81.

3-Benzamido-4,5-O-isopropylidene-2,3,6-trideoxy-L-*ribo*-hexose dimethyl acetal (**10a**): 3.9 g Raney nickel was added to a solution of **9a** (260 mg, 0.53 mmol) in methanol (15 ml) and the suspension was stirred at 60 °C (bath) for an hour. The catalyst was filtered off, washed efficiently with methanol, the filtrate was evaporated at reduced pressure and the residue was purified by column chromatography (hexanes-EtOAc, 65:35) to give **10a** (113 mg, 62.6 %), m.p. 36-38 °C. $[\alpha]_D$ +39.1 (c 0.90, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.34 (d, 3H, H-6), 1.35 and 1.47 (2s, 6H, $C(CH_3)_2$), 1.82-2.16 (m, 2H, H-2), 3.30 and 3.39 (2s, 6H, OCH_3), 4.10-4.48 (m, 3H, H-3, H-4, H-5), 4.60 (dd, 1H, H-1), 6.56 (d, 1H, NH), 7.37-7.80 (m, 5H, ArCH) ppm. Anal. Calcd. for $C_{18}H_{27}NO_5$: C, 64.07, H, 8.07, N, 4.15. Found: C, 63.95, H, 8.01, N, 3.98.

3-Benzamido-4,5-O-isopropylidene-2,3,6-trideoxy-L-*arabino*-hexose dimethyl acetal (**10b**): To a solution of **9b** (846 mg, 1.7 mmol) in ethanol (43 ml) Raney nickel (12.7 g) was added and the mixture was refluxed

for an hour. After filtration through Celite and thorough washing, the filtrate was concentrated under reduced pressure and the residue was purified by chromatography using hexanes-EtOAc (7:3) mixture as eluent to yield **10b** (443 mg, 75.4 %, m.p. 92-3 °C. $[\alpha]_D$ 0.0 (c 0.71, $CHCl_3$). IR: 1640 cm^{-1} (amide-I), 1538 cm^{-1} (amide-II). MS m/e: 322 (M^+ $-CH_3$). ^{1}H NMR ($CDCl_3$): δ 1.29 (d, 3H, H-6), 1.40 and 1.57 (2s, 6H, $C(CH_3)_2$), 1.91-2.02 (m, 2H, H-2), 3.31 and 3.41 (2s, 6H, OCH_3), 4.19-4.52 (m, 3H, H-3, H-4, H-5), 4.53-4.64 (dd, 1H, H-1), 6.57 (d, 1H, NH), 7.38-7.83 (m, 5H, ArCH) ppm. Anal. Calcd. for $C_{18}H_{27}NO_5$: C, 64.07,H, 8.07, N, 4.15. Found: C, 63.83, H, 7.97, N, 4.02.

3-Benzamido-2,3,6-trideoxy-L-*ribo*-hexose (N-Benzoyl-L-ristosamine) (**11a**): A solution of **10a** (83 mg, 0.25 mmol) in acetic acid (2 ml) and water (1 ml) was stirred at 60°C (bath) for an hour. After evaporation of the solvents, the residue was chromatographed with CH_2Cl_2-MeOH (93:7) mixture as eluent, to give **11a** (53.4 mg, 86.0 %). m.p. 125°C, $[\alpha]_D$ -13.1 (c 0.75, EtOH, 10 min), lit.[3]: m.p. 126-8°C, $[\alpha]_D$ -10 (c 0.7, EtOH, 10 min). ^{1}H NMR data are fully consistent with the literature values[11]. **Anal.** Calcd. for $C_{13}H_{17}NO_4$: C, 62.13, H, 6.82, N, 5.57. Found: C, 61.65, H, 6.89, N, 5.59.

3-Benzamido-2,3,6-trideoxy-L-*arabino*-hexose (N-Benzoyl-L-acosamine) (**11b**): **10b** (389 mg, 1.15 mmol) was converted to **11b** (253 mg, 87.3 %) following the procedure described for **11a**. m.p. 214-6°C, $[\alpha]_D$ -44.7 ⟶ -17.9 (equilibrium, c 0.40, EtOH), lit.[12]: m.p. 218-20°C, $[\alpha]_D$ -18.6 (c 0.30, EtOH, 3 h). MS m/e: 252 (M^+ +1), 233 (M^+ $-H_2O$), 215 (M^+- $2H_2O$). The ^{1}H NMR and ^{13}C-NMR spectral data for **11b** agreed with the data in the literature[12]. **Anal.** Calcd. for $C_{13}H_{17}NO_4$: C, 62.13, H, 6.82, N, 5.57. Found: C, 62.45, H, 6.57, N, 5.46.

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