Syntheses of Acyclo-*C*-nucleosides by Ring Transformation of 2(3)-Formyl-glycals [1])

Ivo Rudloff, Klaus Peseke, and Helmut Reinke

Rostock, Fachbereich Chemie der Universität

Abstract. The 2(3)-formyl-glycals **2, 4, 6** react with hydrazine hydrate to furnish the *C*-(1*H*-pyrazol-3-yl)alditoles **7, 8, 9**. Treatment of **2, 4, 6** with cyanoacetamide provides the 2(3)-(2-aminocarbonyl-2-cyano-vinyl)-1,5(2,6)-anhydro-2(3)- deoxy-hex-1-enitols **10, 13, 15**, which are converted into the polyhydroxyalkyl 2-amino-nicotinamides **11, 14, 16** and pyridinecarbonitriles **12**, respectively.

Naturally occurring C-nucleosides such as pyrazofurin, showdomycin, oxazinomycin, and formycin B are important, in part, due to their antibacterial, antiviral, and antitumor properties [1, 2]. On the other hand, there are biologically active C-nucleoside analogues with an open chain sugar fragment [3–5]. Important compounds of this type include the guanosine analogues, acyclovir, which is in clinical use against herpes infections, gancyclovir and the adenosine analogue, (*S*)-9-(2,3-dihydroxy-propyl)adenine.

The development of strategies for the formation of acyclic C-nucleoside analogues is a topic of current interest in organic synthesis [6–9]. This paper describes ring transformations using C-branched, unsaturated sugars with push-pull activation to give C-nucleoside analogues with a polyhydroxyalkyl chain.

Several methods for the synthesis of C-branched sugars are known [10–15]. Recently we have developed a new approach using the reaction of deoxy uloses with carbon disulfide and alkyl halogenides in the presence of sodium hydride to give α-oxoketene dithioacetals with a sugar moiety, such as methyl 4,6-*O*-benzylidene-3-deoxy-3-[bis(methylthio)methylene]-α-D-*erythro*-hexopyranosid-2-ulose and the corresponding 4,6-*O*-benzylidene-2-deoxy-2-[bis(methylthio)methylene]-α-D-*erythro*-hexopyranosid-3-ulose [16, 17]. These *exo*-ene sugars exhibited a push-pull alkene activity that allowed displacement reactions with N-nucleophiles furnishing the corresponding α-oxoketene-*N,S*-acetals [18–20]. Similar push-pull activated, *endo*-unsaturated sugars were prepared by Balasubramanian and his coworkers

[21]. They carried out the reactions of *O*-methyl and *O*-benzyl protected glycals with *N,N*-dimethylformamide and phosphoryl chloride to give the 2-formyl-D-glycals.

We successfully adapted this Vilsmeier-Haack reaction to di-*O*-benzyl-L-rhamnal **3** [22, 23] and tri-*O*-benzyl-D-fructal **5** [23, 24] (Scheme 1). It may be assumed that the protective group at O-4 of **1** is responsible for the significant differences in obtaining of **2** and the


1, 2	R^1	R^2
a	H	BnO
b	BnO	H
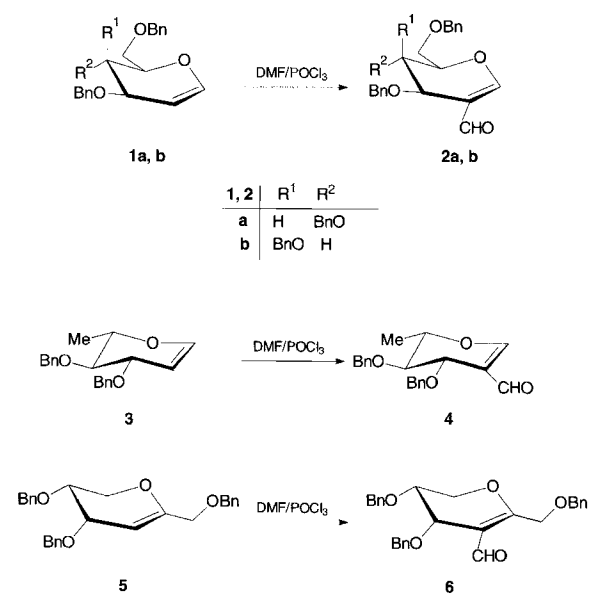
Scheme 1

[1]) Presented in part at the third conference on iminium salts Stimpfach-Rechenberg (Germany), September 17–19, 1997

other formyl-glycals [25]. By means of column chromatography the main products **4** and **6** could be separated as syrups. The structures of which were established mainly by NMR measurements. The absence of signals for 2-H and 3-H, respectively, and the appearance of the formyl proton signals at $\delta = 9.30$ and 9.87 ppm indicated the successful formylation. As expected the signals for the formyl group in the ^{13}C NMR spectra were found in the typical range for carbonyl atoms at $\delta = 190.4$ and 188.5 ppm, respectively.

When the formyl glycals **2a**, **2b** and **4** are treated with hydrazine hydrate in refluxing ethanol, the *C*-(1*H*-pyrazol-4-yl)alditoles **7a**, **7b** and **8** were obtained in high yields. According to similar push-pull alkenes the nucleophilic attack of hydrazine will most likely be initiated at C-1, followed by cyclization involving the formyl group to furnish the corresponding pyrazole [18–20] (Scheme 2).

The structures of **7a**, **7b** and **8** were verified by NMR data and elemental analysis. While no carbonyl signals were observed, two additional proton signals appeared, caused by the OH and NH groups. On the other hand, signals of pyrazole C-3,5 in the typical range for heteroaromatic atoms at $\delta = 133.4$ ppm (**7a**, **7b**) and at $\delta = 127.0–139.5$ ppm (**8**, together with phenyl signals) indicated the successful ring transformation. Generally, another tautomeric pyrazole structures could be formulated for the products. It is assumed, however, that there exists a fast equilibrium between both tautomers in solution as is typical for pyrazole derivatives.
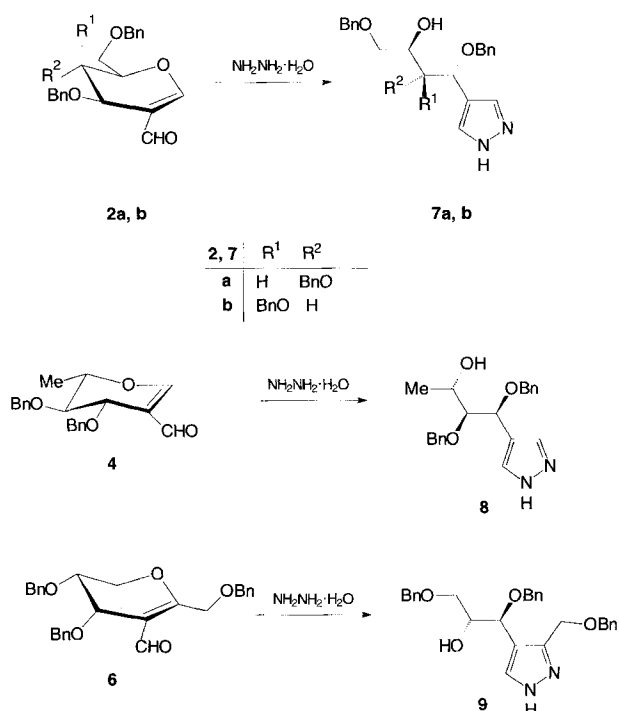
Similarly, the ring transformation of 3-formyl-1,4,5-tri-*O*-benzyl-D-fructal (**6**) with hydrazine hydrate afforded **9** in 88% yield, which is an alditol structure integrating a pyrazole ring.

In addition, treatment of 2-formyl-glycals **2a**, **2b** with cyanoacetamide under Knoevenagel-Cope conditions [26] and with piperidinium acetate, as the most effective catalyst afforded the branched chain sugars **10a**, **10b**. By means of the NMR spectra only one (*E*) and (*Z*) isomer was detected. However, the data did not permit any decision, which of these compounds had been formed.

Compounds **10a**, **10b** may be regarded as push-pull butadienes [27–29], that could allow a displacement reaction of pyranose ring oxygen with ammonia including a ring transformation through nitrile cyclization, offering a good way to prepare pyridine acyclo-*C*-nuleosides. Thus, when **10a**, **10b** were treated with ammonia in ethanol the nicotinamide derivatives **11a**, **11b** were formed as colorless crystals in good yields (Scheme 3).


2a, b   **10a, b**

11a, b   **12a, b**

2, 10, 11, 12	R^1	R^2
a	H	BnO
b	BnO	H
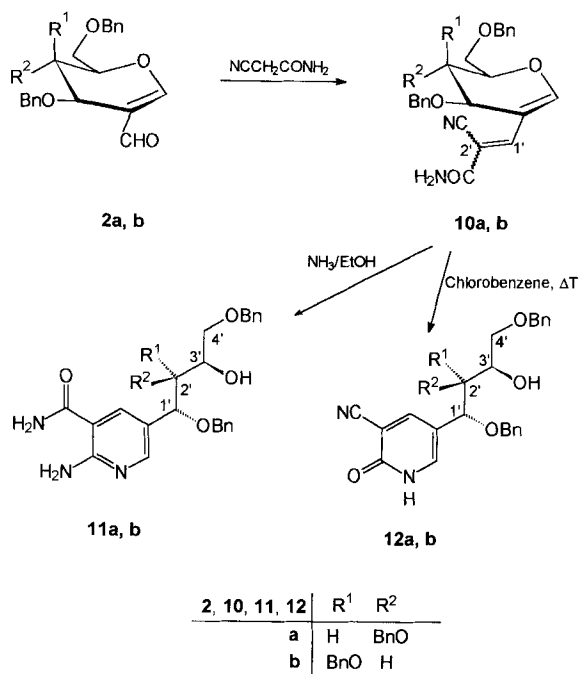
Scheme 3

The structures were determined by IR, NMR studies and elemental analysis. Since IR spectra did not indicate a cyano band, the ring closure reaction could be assumed.

On the other hand, the prolongation of the reaction of 2-formyl-glycals **2a**, **2b** with cyanoacetamide in presence of piperidinium acetate furnished by an intramolecular ring transformation of the branched chain sugars **10a**, **10b** the pyridones **12a**, **12b**. The IR spectra of

2a, b   **7a, b**

2, 7	R^1	R^2
a	H	BnO
b	BnO	H

4

8

6

9

Scheme 2

these compounds show the cyano band. Furthermore, the structure was established by NMR measurements. The lack of the signals for the carbonyl group and the appearance of a OH signal indicated the existence of the hydroxypyridine tautomer in solution.

Finally, the treatment of 2-formyl-rhamnal **4** and 3-formyl-D-fructal **6** with cyanoacetate in boiling toluene in the presence of piperidinium acetate furnished the corresponding 3-(glycosen-2 (or 3)yl)acrylamides **13** and **15** (Scheme 4).
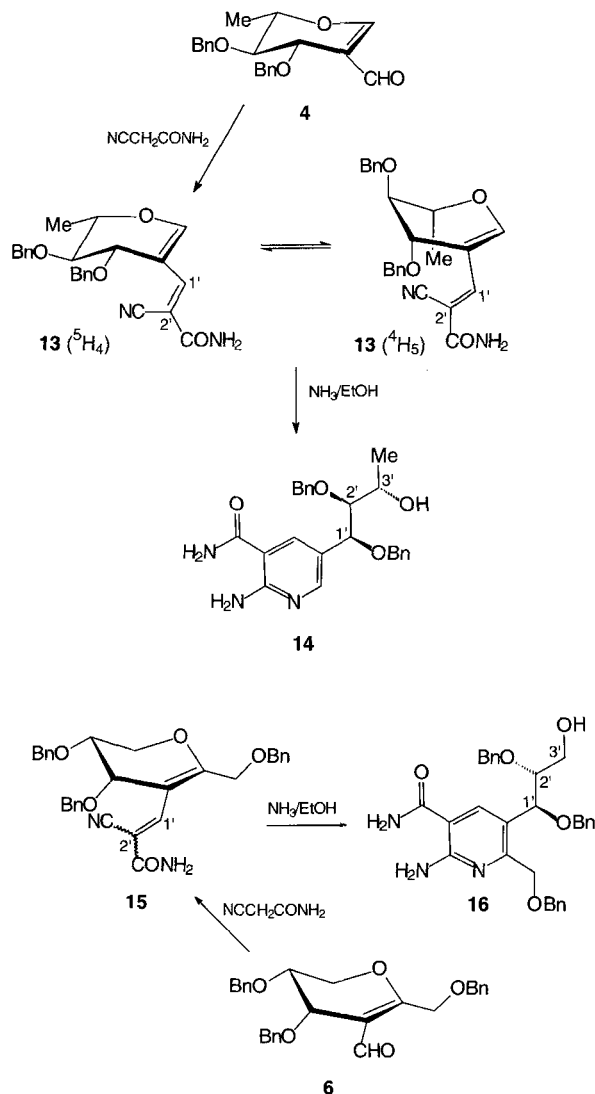
Scheme 4

The structures of **13** and **15** were determined by IR and NMR studies. Although no formyl signals were observed, an additional cyano signal appeared.

The crystallographic data were in agreement with the (*E*)-configuration and the $^4H_5$-conformation of **13**. A complete conjugation in the π system caused a planar

arrangement between O-1 and C-9 and between O-1 and C-10, respectively. The reduced C–C distances of O-1-C-1 and C-2-C-7 (133.5 and 144.4 pm) showed the push-pull butadiene character. On the other side the increase of bond lengths of C-1-C-2 and C-7-C-8 (134.4 and 135 pm) was not as high as expected. Due to the free rotation around the single bond a disordering in the benzyl group at O-3 was observed. In Fig. 1 only one position of the benzyl group at O-3 is shown for clearness. Intermolecular hydrogen bonds N-H-N and N-H-O caused an infinite chain of molecules parallel to the b axis. The middle distances N–O were 287 pm and N–N 303 pm. The angles N-H-O 136° and N-H-N 158° were indicated.
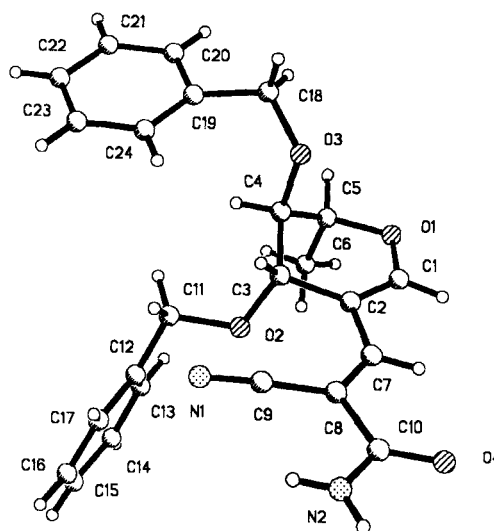

Fig. 1 Crystallographic structure of compound **13**

The compounds **13** and **15** react with ammonia, by heating in aqueous ethanol, to furnish through ring transformation of the pyran ring, the expected 2-amino-nicotinamides **14** and **16** in yields of 72 and 82%. The absence of cyano bands in the IR spectra and the characteristic shifts of pyridine signals verify the nicotinamide structures.

Experimental

Melting points were determined with a Boëtius melting point apparatus and have been corrected. Specific rotations were determined with a Polar LµP (IBZ Messtechnik). IR spectra were recorded with a Nicolet 205 FT-IR spectrometer. ^1H NMR (300.133 MHz and 250.133 MHz, respectively) and ^{13}C NMR (75.466 MHz and 62.896 MHz, respectively) were obtained on Bruker instruments WM 300 and AC 250, respectively. The ^{13}C NMR spectra were determined by DEPT

and/or ^{1}H, ^{13}C, COSY experiments. ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to the solvent signal. The mass spectra were recorded on an AMD 402/3 spectrometer. For column chromatography Merck Silica gel 60 (63–200 mesh) was used. TLC was performed on silica gel 60 GF$_{254}$ (Merck) with detection by UV light (λ = 254 nm) and/or by charing with 5% sulfuric acid in methanol. Elemental analyses was carried out on a Leco CHNS-932.

Synthesis of Formyl-glycales

1,5-Anhydro-3,4,6-tri-O-benzyl-2-deoxy-2-formyl-D-arabino-hex-1-enitol (**2a**) and *1,5-Anhydro-3,4,6-tri-O-benzyl-2-deoxy-2-formyl-D-lyxo-hex-1-enitol* (**2b**) were prepared according to a literature procedure [21].

1,5-Anhydro-3,4-di-O-benzyl-2,6-deoxy-2-formyl-L-erythro-hex-1-enitol (**4**)

To a solution of 3,4-Di-O-benzyl-L-rhamnal (**3**) (5 g, 16 mmol) in dry N,N-dimethyl formamide (32 ml), under exclusion of moisture, was dropwise added phosphoryl chloride (7.43 g, 4.44 ml, 48 mmol) at 0 °C. After stirring for 8 h at 22 °C the redbrown solution was poured into ice water (100 ml), neutralized to pH 7 with 0.1M aqueous NaOH and extracted with diethyl ether (2 × 150 ml). The combined organic phases were washed with water, dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The obtained syrup was chromatographed (toluene-ethyl acetate 9:1). Yield 2.7g (49.5%), colorless syrup, $[\alpha]_D^{22}$ = + 44.7 (c = 1, CHCl$_3$), R_f = 0.42 (toluene-ethyl acetate 9:1). – IR (neat): v/cm^{-1} = 1673 (CHO), 1627 (C=C). – ^{1}H NMR(250 MHz, CDCl$_3$): δ/ppm = 1.39 (d, 3H, ^3J = 7.02 Hz, CH$_3$), 3.60 (t, 1H, $^3J_{4,3}$ = 4.88 Hz, $^3J_{4,5}$ = 2.44 Hz, 4-H), 4.40 (m, 2H, ^2J = 11.9 Hz, 3-H, 1CHHPh), 4.48–4.63 (m, 3H, 5-H, 2CHHPh), 4.72 (d, 1H, ^2J = 11.6 Hz, 1CHHPh), 7.18–7.38 (m, 11H, 1-H, Ph), 9.30 (s, 1H, CHO). – ^{13}C NMR(250 MHz, CDCl$_3$): δ/ppm = 16.8 (CH$_3$), 66.2 (C-4), 71.6, 72.6 (CH$_2$Ph), 74.8 (C-3), 76.8 (C-5), 117.5 (C-2), 127.6–138.5 (Ph), 164.4 (C-1), 190.4 (CHO). – MS (CI-Isobutane): m/e (%) = 339 (8) (MH$^+$), 230 (87) (M–OCH$_2$Ph).

C$_{21}$H$_{21}$O$_4$ calcd: C 74.76 H 6.27
(338.40) found: C 74.46 H 6.11.

2,6-Anhydro-1,4,5-tri-O-benzyl-3-deoxy-3-formyl-D-erythro-hex-2-enitol (**6**)

1,4,5-Tri-O-benzyl-D-fructal (**5**)(5 g, 12 mmol) [4,3] was transformed to **6** by treatment with phosphoryl chloride (5.52 g, 3.34 ml, 36 mmol) in N,N-dimethylformamide (24 ml) as described above. Yield 2.5 g (47%), colorless syrup, $[\alpha]_D^{22}$ = + 144.6 (c = 1, CHCl$_3$), R_f = 0.38 (toluene-ethyl acetate 9:1). – IR (neat): v/cm^{-1} = 1660 (CHO), 1620 (C=C). – ^{1}H NMR (250 MHz, CDCl$_3$): δ/ppm = 3.62 (ddd, 1H, $^3J_{5,4}$ = 3.05 Hz, 5-H), 4.18–4.34 (m, 3H, $^2J_{6a,6b}$ = 12.52 Hz, 6a-H, 2CHHPh), 4.43 (d, 1H, 6b-H), 4.56 (m, 3H, ^2J = 11.9 Hz, 3CHHPh), 4.79 (dd, 1H, ^4J = 1.53 Hz, 4-H), 4.84 (d, 1H, ^2J = 11.29 Hz, 1CHHPh), 7.20–7.45 (m, 16H, 2-H, Ph), 9.87 (s, 1H, CHO). – ^{13}C NMR (250 MHz, CDCl$_3$): δ/ppm = 64.1 (C-1), 64.7 (C-5), 66.3 (C-6), 71.2 (CH$_2$Ph), 72.6 (C-4), 73.4, 73.6 (2CH$_2$Ph), 115.7 (C-3), 127.5–138.9 (Ph), 169.9 (C-2), 188.5 (CHO). –

MS (CI-Isobutane): m/e (%) = 445 (1) (MH$^+$), 337 (69) (M–OCH$_2$Ph).
C$_{28}$H$_{28}$O$_5$ calcd: C 75.66 H 6.35
(444.53) found: C 75.39 H 6.39.

Ringtransformations into Pyrazoles

A mixture of formyl glycals **2, 4, 6** (2.25 mmol) and hydrazine hydrate (0.25 g, 4.50 mmol) in ethanol (20 ml) was heated under reflux for 30 min. Solvent evaporation, recrystallization of the solid residue or column chromatography (chloroform-methanol 9:1) furnished the corresponding pyrazoles.

1,2,4-Tri-O-benzyl-1C-(1H-pyrazol-4-yl)-D-arabino-tetritol (**7a**)

Yield 0.95 g (92%), colorless syrup, $[\alpha]_D^{22}$ = −27.9 (c = 1, CHCl$_3$), R_f = 0.375 (chloroform-ethyl acetate 9:1). – IR (KBr): v/cm^{-1} = 3490 (br, NH, OH). – ^{1}H NMR(250 MHz, [D6] DMSO): δ/ppm = 3.46 (dd, 1H, $^2J_{4a,4b}$ = 9.92 Hz, $^3J_{4,3}$ = 6.11 Hz, 4a-H), 3.70 (m, 2H, $^3J_{2,1}$ = 5.34 Hz, 2-H, 4b-H), 3.76 (m, 1H, 3-H), 4.30 (d, 1H, ^2J = 11.83 Hz, 1CHHPh), 4.36–4.45 (m, 4H, 4CHHPh), 4.55 (d, 1H, 1CHHPh), 4.73 (1H, d, 1-H), 4.87 (1H, d, ^3J = 5.34 Hz, OH), 7.00–7.35 (m, Ph, NH), 7.45 (s, 2H, pyrazole 3-H, 5-H). – ^{13}C NMR(250 MHz, [D6] DMSO): δ/ppm = 69.8 (C-3), 70.1, 72.5, 74.3 (3CH$_2$Ph), 71.7 (C-4), 73.9 (C-1), 84.7 (C-2), 118.6 (pyrazole C-4), 127.3–139.1 (Ph), 133.4 (pyrazole C-3, C-5). – MS (CI-Isobutane): m/e (%) = 459 (28) (MH$^+$), 351 (16) (M–OCH$_2$Ph).
C$_{28}$H$_{30}$N$_2$O$_4$ calcd: C 73.34 H 6.59 N 6.11
(458.56) found: C 73.07 H 6.63 N 6.18.

1,2,4-Tri-O-benzyl-1C-(1H-pyrazol-4-yl)-D-lyxo-tetritol (**7b**)

Yield 0.88 g (85%), m.p. 83 °C (diethyl ether/n-heptane), colorless needles, $[\alpha]_D^{22}$ = + 54.5 (c = 1 , CHCl$_3$), R_f = 0.374 (chloroform-ethyl acetate 9:1). – IR (KBr): v/cm^{-1} = 3492 (br, OH, NH). – ^{1}H NMR (250 MHz, [D6] DMSO): δ/ppm = 3.42 (ddd, 2H, $^2J_{4a,4b}$ = 10.07 Hz, $^3J_{4,3}$ = 5.8 Hz, 4a,b-H), 3.70 (dd, 2H, $^3J_{2,1}$ = 6.41 Hz, $^3J_{2,3}$ = 3.05 Hz, 2-H), 3.95 (m, 1H, 3-H), 4.19 (d, 1H, 1CHHPh), 4.29–4.45 (m, 5H, 5 CHHPh), 4.59 (1H, d, 1-H), 4.65 (1H, d, ^3J = 7.0 Hz, OH), 7.05–7.40 (m, Ph, NH), 7.60 (s, 2H, pyrazole 3-H, 5-H). – ^{13}C NMR (250 MHz, [D6] DMSO): δ/ppm = 69.7 (C-3), 70.6, 73.4, 74.5 (3CH$_2$Ph), 71.3 (C-4), 73.5 (C-1), 81.6 (C-2), 119.2 (pyrazole C-4), 127.8–138.1 (Ph), 133.4 (pyrazole C-3, C-5). – MS (CI-Isobutane): m/e (%) = 459 (36) (MH$^+$), 351 (54) (M–OCH$_2$Ph).
C$_{28}$H$_{30}$N$_2$O$_4$ calcd: C 73.34 H 6.59 N 6.11
(458.56) found: C 73.36 H 6.59 N 6.08.

1,2-Di-O-benzyl-4-deoxy-1C-(1H-pyrazol-4-yl)-L-arabino-tetritol (**8**)

Yield 0.75 g (90%), m.p. 138–139° (acetone/diethyl ether), white solid, $[\alpha]_D^{22}$ = + 43.8 (c = 1.0, CHCl$_3$), R_f = 0.45 (chloroform-methanol 9:1). – IR (KBr): v/cm^{-1} = 3280 (br, OH, NH). – ^{1}H NMR (250 MHz, [D6] DMSO): δ/ppm = 1.06 (d, 3H, $^3J_{4,3}$ = 6.1 Hz, CH$_3$), 3.61 (m, 2H, $^3J_{2,1}$ = 3.96 Hz, 2-H, 3-H), 4.35 (dd, 2H, 2CHHPh), 4.55 (m, 1H, 1-H), 4.65 (dd, 2H, 2CHHPh), 7.20–7.40 (m, Ph, NH), 7.62 (s, 2H, pyrazole 3-H, 5-H). – ^{13}C NMR (250 MHz, [D6] DMSO): δ/ppm = 17.9 (CH$_3$), 66.3 (C-3), 69.7, 74.2 (2CH$_2$), 74.5 (C-

2), 86.8 (C-1), 118.6 (pyrazole C-4), 127.0–139.5 (Ph, pyrazole C-3, C-5). – MS (CI-Isobutane): m/e (%) = 353 (70) (MH$^+$), 245 (45) (M–OCH$_2$Ph).

$C_{21}H_{24}N_2O_3$ calcd: C 71.57 H 6.86 N 7.95
(352.43) found: C 71.77 H 6.91 N 7.86.

1,3-Di-O-benzyl-1C-(3-benzyloxymethyl-1H-pyrazol-4-yl)-D-erythro-glycerol (**9**)

Yield 0.91 g (88%), m.p. 140–141 °C (ethyl acetate), white solid, $[\alpha]_D^{22}$ = + 40.6 (c = 1.0, DMSO). – IR (KBr): v/cm^{-1} = 3120–3288 (OH, NH), R_f = 0.50 (chloroform-methanol 9:1). – ^{1}H NMR (250 MHz, [D6] DMSO): δ/ppm = 3.49 (m, 2H, $^2J_{3a,3b}$ = 11.60 Hz, 3a-H, 3b-H), 3.73 (m, 1H, $^3J_{2,1}$ = 4.58 Hz, 2-H), 4.30 (d, 1H, ^2J = 11.9 Hz, 1CHHPh), 4.47 (m, 6H, 3CH$_2$), 4.61 (d, 1H, 1CHHPh), 4.68 (d, 1H, H-1), 7.16–7.35 (m, Ph, NH), 7.59 (s, 1H, 3-H). – ^{13}C NMR (250 MHz, [D6] DMSO): δ/ppm = 61.1, 63.3, 69.8, 71.5, 72.3 (5CH$_2$), 73.3 (C-2), 83.0 (C-1), 116.4 (pyrazole C-4), 127.3–139.3 (Ph, pyrazole C-3, C-5). – MS (CI-Isobutane): m/e (%) = 459 (1) (MH$^+$), 351 (26) (M–OCH$_2$Ph).

$C_{28}H_{30}N_2O_4$ calcd: C 73.34 H 6.59 N 6.11
(458.56) found: C 73.16 H 6.55 N 6.31.

Knoevenagel Reaction with Cyanoacetamide

2-(2-Aminocarbonyl-2-cyano-vinyl)-1,5-anhydro-3,4,6-tri-O-benzyl-2-deoxy-D-arabino-hex-1-enitol (**10a**)

Under vigorous stirring or with a help of ultrasound 0.5 g (6.0 mmol) cyanoacetamide were suspended in a solution of **2a** (1.33 g, 3.0 mmol), acetic acid (0.1 ml, 1.7 mmol) and piperidine (0.05 ml, 0.51 mmol) in toluene (20 ml). The mixture was heated at reflux under a Dean-Stark trap for 30 min. After removal of the solvent the resulting crude syrup was purified by elution from a silica gel column (20 cm) with chloroform-ethyl acetate 5:2 to provide 1.0 g (65%) **10a**, as a yellowish syrup, $[\alpha]_D^{22}$ = + 13.7 (c = 1, CHCl$_3$). – IR (KBr): v/cm^{-1} = 2207 (CN), 1685 (C=O), 1602, 1573 (C=C). – ^{1}H NMR (250 MHz, CDCl$_3$): δ/ppm = 3.50 (dd, 1H, $^2J_{6a,6b}$ = 10.99 Hz, $^3J_{6a,5}$ = 4.27 Hz, 6a-H), 3.67 (dd, 1H, $^3J_{6b,5}$ = 7.94 Hz, 6b-H), 4.03 (t, 1H, $^3J_{4,3}$ = 2.14 Hz, $^3J_{4,5}$ = 4.58 Hz, 4-H), 4.28–4.41 (m, 3H, 3CHHPh), 4.58 (s, 2H, 2CHHPh), 4.65 (m, 1H, 5-H), 4.78 (dd, 2H, ^2J = 10.37 Hz, 3-H, 1CHHPh), 6.05 (s, 2H, NH$_2$), 7.10–7.26 (m, 16H, 1-H, Ph), 7.70 (s, 1H, 1'-H). – ^{13}C NMR (250 MHz, CDCl$_3$): δ/ppm = 52.9 (CH$_3$), 67.8 (C-3), 68.1 (C-6), 68.4 (C-4), 69.7, 71.7, 73.4 (3CH$_2$Ph), 77.2 (C-5), 95.6 (C-2'), 111.1 (C-2), 118.1 (CN), 127.7–137.4 (Ph), 153.1 (C-1'), 160.1 (C-1), 163.4 (C=O). – MS (CI-Isobutane): m/e (%) = 511 (35) (MH$^+$), 403 (100) (M–OCH$_2$Ph).

$C_{31}H_{30}N_2O_5$ calcd: C 72.92 H 5.92 N 5.49
(510.59) found: C 73.19 H 6.06 N 5.38.

2-(2-Aminocarbonyl-2-cyano-vinyl)-1,5-anhydro-3,4,6-tri-O-benzyl-2-deoxy-D-lyxo-hex-1-enitol (**10b**)

The reaction of **2b** with cyanoacetamide was carried out as described above. Yield 1.0 g (58%), white solid, m.p. 124 °C (diethyl ether/n-heptane), $[\alpha]_D^{22}$ = + 36.7° (c = 1, CHCl$_3$). – IR (KBr): v/cm^{-1} = 2211 (CN), 1687 (C=O), 1598, 1578 (C=C). – ^{1}H NMR (250 MHz, CDCl$_3$): δ/ppm = 3.50 (dd, 1H, $^2J_{6a,6b}$ = 10.67 Hz, $^3J_{6a,5}$ = 5.19 Hz, 6a-H), 3.67 (dd, 1H, $^3J_{6b,5}$ = 7.63 Hz, 6b-H), 4.03 (t, 1H, $^3J_{4,3}$ = 2.14 Hz, $^3J_{4,5}$ = 4.58 Hz,

4-H), 4.28–4.41 (m, 3H, 3CHHPh), 4.58 (s, 2H, 2 CHHPh), 4.65 (m, 1H, 5-H), 4.78 (dd, 2H, ^2J = 10.37 Hz, 3-H, 1CHHPh), 7.10–7.26 (m, 16H, 1-H, Ph), 7.61 (s, 1H, 1'-H). – ^{13}C NMR (250 MHz, CDCl$_3$): δ/ppm = 52.9 (Me), 67.8 (C-3), 68.1 (C-6), 68.4 (C-4), 69.7, 71.7, 73.4 (3CH$_2$Ph), 78.0 (C-5), 96.3 (C-2'), 112.7 (C-2), 118.1 (CN), 127.7–138.3 (Ph), 152.0 (C-1'), 159.3 (C-1), 163.0 (C=O). – MS (CI-Isobutane): m/e (%) = 511 (12) (MH$^+$), 403 (38) (M–OCH$_2$Ph).

$C_{31}H_{30}N_2O_5$ calcd: C 72.92 H 5.92 N 5.49
(510.59) found: C 73.07 H 5.76 N 5.46.

2-[(E)-2-Aminocarbonyl-2-cyano-vinyl)]-1,5-anhydro-3,4-di-O-benzyl-2,6-dideoxy-L-erythro-hex-1-enitol (**13**)

Compound **4** (1.01 g, 3.0 mmol) was treated with cyanoacetamide (0.5 g, 6.0 mmol) as described for preparation of **10a**. Yield 0.84 g (69%), m. p. 130–132 °C (diethyl ether/n-heptane), colorless crystals, $[\alpha]_D^{22}$ = + 56.9° (c = 1, CHCl$_3$), R_f = 0.30 (chloroform-ethyl acetate 9:1). – IR (KBr): v/cm^{-1} = 3462, 3352, 3192 (NH$_2$), 2207 (CN), 1678 (C=O), 1601, 1571 (C=C). – ^{1}H NMR (250 MHz, CDCl$_3$): δ/ppm = 1.35 (d, 3H, ^3J = 7.32 Hz, CH$_3$), 3.82 (t, 1H, $^3J_{4,3}$ = 4.88 Hz, 4-H), 4.42 (d, 1H, ^2J = 10.68 Hz, 1CHHPh), 4.60 (m, 3H, 5-H, 2CHHPh), 4.70 (t, 1H, 3-H), 4.80 (d, 1H, 1CHHPh), 7.18 (s, 2H, NH$_2$), 7.20–7.32 (m, 16H, 1-H, Ph), 7.74 (s, 1H, 1'-H). – ^{13}C NMR (250 MHz, CDCl$_3$): δ/ppm = 16.7 (CH$_3$), 68.4 (C-3), 69.5, 71.5 (2CH$_2$Ph), 71.3 (C-4), 75.3 (C-5), 95.1 (C-2'), 111.0 (C-2), 116.6 (CN), 127.7–137.7 (Ph), 153.6 (C-1'), 160.4 (C-1), 163.5 (C=O). – MS (CI-Isobutane): m/e (%) = 405 (15) (MH$^+$), 297 (100) (M–OCH$_2$Ph).

$C_{24}H_{24}N_2O_4$ calcd: C 71.20 H 5.94 N 6.93
(404.50) found: C 71.07 H 5.91 N 6.70.

Compound **13** was subjected to X-ray analysis at 293 K. The structure was solved by direct methods with the assistance of Siemens SHELXTL and refined with SHELXL-93. All non-hydrogen atoms were refined anisotropically, hydrogens introduced at theoretical positions and refined according to the riding model. **13**, ($C_{24}H_{24}N_2O_4$); MW = 404.5; crystal size (mm): 0.5 × 0.34 × 0.26; space group P2$_1$; Z = 2; monoclinic; a = 1130.3(2) pm; b = 860.3(10) pm; c = 1168.5(2) pm; α = 90°; β = 101.71°; γ = 90°; V = 1112.6 × 10^6 pm^3; d = 1.207 Mg m^{-3}; F(000) = 428; μ = 0.83 cm^{-1}; ω-scan 3.6 ≤ 2Θ ≤ 44; 3087 reflections collected; 2232 observed reflections (I > 2σ(I)). R_F (I > 2σ(I)) = 4.90%; R_F (all data) = 6.40%. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 101293. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. Code +(1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk).

2-(2-Aminocarbonyl-2-cyano-vinyl)-2,6-anhydro-1,4,5-tri O-benzyl-3-deoxy-D-threo-hex-2-enitol (**15**)

Compound **6** (1.33 g, 3.0 mmol) was treated with cyanoacetamide (0.5 g, 6.0 mmol), as described for preparation of **10a**. Yield 0.85 g (55%), colorless syrup, $[\alpha]_D^{22}$ = + 118.9° (c = 0.65, CHCl$_3$), R_f = 0.51 (chloroform-ethyl acetate 9:1). – IR (Neat): v/cm^{-1} =3468, 3353, 3193 (NH$_2$), 2206 (CN), 1687 (C=O), 1568 (C=C). – ^{1}H NMR (250 MHz, CDCl$_3$): δ/ppm =

3.73 (ddd, 1H, $^3J_{5,4}$ = 2.7 Hz, $^3J_{5,6a}$ = 4.3 Hz, $^3J_{5,6b}$ = 7.3 Hz, 5-H), 4.02 (d, 1H, $^2J_{1a,2a}$ = 12.8 Hz, 1a-H), 4.13 (ddd, 1H, $^2J_{6a,6b}$ = 10.4 Hz, 6a-H), 4.24–4.35 (m, 2H, 1b-H, 6b-H), 4.45 (dd, 2H, ^2J = 11.6 Hz, 2CHHPh), 4.58 (d, 1H, 1CHHPh), 4.69 (d, 1H, 1CHHPh), 4.94 (d, 1H, ^2J = 10.7 Hz, 1CHHPh), 5.04 (d, 1H, 1CHHPh), 5.19 (d, 1H, 4-H), 6.13 (s, 2H, NH$_2$), 7.19–7.34 (m, 1-H, Ph), 8.22 (s, 1H, 2'-H). – ^{13}C NMR (CDCl$_3$): δ/ppm = 62.1 (C-1), 68.0 (C-6), 68.2 (C-4), 72.1, 72.8, 73.5 (3 × CH$_2$Ph), 77.2 (C-5), 96.2 (C-2'), 110.1 (C-3), 118.4 (CN), 127.0–138.8 (Ph), 149.7 (C-2), 163.6 (C-1'), 167.1 (C=O). – MS (CI-Isobutane): m/e (%) = 511 (5) (MH$^+$), 403 (33) (M – OCH$_2$Ph).
C$_{31}$H$_{30}$N$_2$O$_5$ calcd: C 72.92 H 5.92 N 5.49
(510.59)   found: C 72.79 H 6.13 N 5.57.

Ring Transformation of 2(3)-(2-Aminocarbonyl-2-cyanovinyl)glycals with Ammonia

2.0 mmol of **10, 13, 15** were dissolved in hot ethanol (20 ml). At 50 °C 25% aqueous ammonia solution (0.4 ml, 6 mmol) was added and the mixture was stirred for 15 min at room temperature. Then it was heated at reflux for further 30 min. Solvent was evaporated and the residue was purified by column chromatography (chloroform-ethyl acetate 1:1).

2-Amino-5-(1,2,4-tri-O-benzyl-D-arabino-1,2,3,4-tetrahydroxy-butyl)pyridine-3-carboxamide (**11a**)

Yield 0.83 g (79%), *m. p.* 64–66 °C (diethyl ether), colorless crystals, $[\alpha]_D^{22}$ = + 9.66° (c = 1, CHCl$_3$), R_f = (chloroform-methanol 9:1). – IR (KBr): ν/cm^{-1} = 3454, 3343, 3100 (NH$_2$, OH), 1662, 1621, (C=O, NH$_2$), 1572, 1556 (C=C). – ^{1}H NMR (300 MHz, CDCl$_3$): δ/ppm = 3.50 (dd, 1H, $^2J_{2',1'}$ = 3.1 Hz, $^3J_{2',3'}$ = 7.3 Hz, 2'-H), 3.57 (d, 2H, $^3J_{4',3'}$ = 4.6 Hz, 4'a,b-H), 3.98 (m, 1H, 3'-H), 4.05 (d, 1H, ^2J = 11.1 Hz, 1CHHPh), 4.16 (d, 1H, 1CHHPh), 4.32–4.45 (m, 4H, ^2J = 11.4 Hz, 4CHHPh), 4.56 (d, 1H, 1'-H), 5.73 (s, 2H, NH$_2$), 6.65 (s, 2H, CONH$_2$), 7.00–7.39 (Ph), 7.71 (d, 1H, $^3J_{4,6}$ = 2.2 Hz, 4-H), 7.95 (d, 1H, 6-H). – ^{13}C NMR (300 MHz, CDCl$_3$): δ/ppm = 69.1 (C-1'), 70.1, 70.6, 72.5, 73.5 (4CH$_2$), 76.5 (C-2'), 81.2 (C-3'), 107.8 (C-3), 121.2 (C-5), 126.9–136.5 (Ph), 136.7 (C-4), 150.1 (C-6), 157.9 (C-2), 168.9 (C=O). – MS (CI-Isobutane): m/e (%) = 528 (14) (MH$^+$), 420 (45) (M – OCH$_2$Ph).
C$_{31}$H$_{33}$N$_3$O$_5$ calcd: C 70.57 H 6.25 N 7.96
(527.62)   found: C 70.29 H 6.34 N 7.87.

2-Amino-5-(1,2,4-tri-O-benzyl-D-lyxo-1,2,3,4-tetrahydroxy-butyl)pyridine-3-carboxamide (**11b**)

Yield 0.72 g (68%), colorless syrup, $[\alpha]_D^{22}$ = – 31.3° (c = 0.5, CHCl$_3$), R_f = 0.35 (chloroform-methanol 9:1). – IR (KBr): ν/cm^{-1} = 3111, 3311, 3422 (NH$_2$, OH),), 1625, 1670 (C=O, NH$_2$), 1567, 1553 (C=C). – ^{1}H NMR (300 MHz, CDCl$_3$): δ/ppm = 3.40 (ddd, 2H, $^2J_{4a',4b'}$ = 9.5 Hz, $^3J_{4a',3'}$ = 3.4 Hz, $^3J_{4b',3'}$ = 6.1 Hz, 4'a,b-H), 3.57 (dd, 1H, $^3J_{2',1'}$ = 7.3 Hz, 2'-H), 4.04 (m, 2H, 3'-H, 1CHHPh), 4.30 (dd, 2H, ^2J = 11.1 Hz, 2CHHPh), 4.37 (m, 2H, 1'-H, 1CHHPh), 4.45 (dd, 2H, ^2J = 11.8 Hz, 2CHHPh), 4.56 (d, 1H, 1'-H), 5.50 (s, 2H, NH$_2$), 6.47 (s, 2H, CONH$_2$), 6.93–7.30 (Ph), 7.48 (d, 1H, $^3J_{4,6}$ = 2.3 Hz, 4-H), 8.08 (d, 1H, 6-H). – ^{13}C NMR (300 MHz, CDCl$_3$): δ/ppm = 68.5 (C-1'), 69.9, 70.2, 72.6, 73.5 (4CH$_2$), 77.1 (C-2'), 80.3

(C-3'), 107.3 (C-3), 121.8 (C-5), 126.9–136.5 (Ph), 136.8 (C-4), 151.1 (C-6), 157.9 (C-2), 168.7(C=O). – MS (CI-Isobutane): m/e (%) = 528 (12) (MH$^+$), 420 (36) (M – OCH$_2$Ph).
C$_{31}$H$_{33}$N$_3$O$_5$ calcd: C 70.57 H 6.25 N 7.96
(527.62)   found: C 70.38 H 6.30 N 7.91.

2-Amino-5-(1,2-di-O-benzyl-L-arabino-4-deoxy-1,2,3-trihy-droxy-butyl)pyridine-3-carboxamide (**14**)

0.77 g (2.0 mmol) of **13** were treated with 25% aqueous ammonia solution (0.4 ml, 6.0 mmol), as described for preparation of **11a,b**. Yield 0.58 g (72%), colorless syrup, $[\alpha]_D^{22}$ = + 136.0° (c = 0.5, CHCl$_3$), R_f = 0.30 (chloroform-methanol 9:1). – IR (Neat): ν/cm^{-1} = 3300, 3432, 3150 (NH$_2$, OH), 1670, 1628 (C=O, NH$_2$), 1559, 1576 (C=C). – ^{1}H NMR (300 MHz, CDCl$_3$): δ/ppm = 1.13 (d, 3H, ^3J = 6.5 Hz, CH$_3$), 3.30 (q, 1H, $^3J_{2',1'}$ = 3.8 Hz, $^3J_{2',3'}$ = 6.1 Hz, 2'-H), 3.82 (m, 1H, 3'-H), 4.18 (d, 1H, ^2J = 11.8 Hz, 1CHHPh), 4.29 (d, 1H, 1CHHPh), 4.40–4.56 (m, 3H, 1'-H, 2CHHPh), 5.68 (s, 2H, NH$_2$), 6.54 (s, 2H, CONH$_2$), 7.08–7.34 (Ph), 7.69 (d, 1H, $^4J_{4,6}$ = 1.9 Hz, 4-H), 7.99 (d, 1H, 6-H). – ^{13}C NMR (300 MHz, CDCl$_3$): δ/ppm = 19.9 (CH$_3$), 67.6 (C-1'), 71.2, 74.8 (2CH$_2$Ph), 78.2 (C-2'), 85.8 (C-3'), 109.2 (C-3), 122.2 (C-4), 128.2–138.3 (Ph), 137.2 (C-3), 152.0 (C-5), 159.4 (C-2), 170.3 (C=O). – MS (CI-Isobutane): m/e (%) = 422 (12) (MH$^+$), 314 (53) (M – OCH$_2$Ph).
C$_{24}$H$_{27}$N$_3$O$_4$ calcd: C 68.32 H 6.40 N 9.96
(421.53)   found: C 68.14 H 6.32 N 9.88.

2-Amino-6-benzyloxymethyl-5-(1,2-di-O-benzyl-D-erythro-1,2,3-trihydroxy-propyl)pyridine-3-carboxamide (**16**)

Yield 0.86 g (82%), *m.p.* 117–119 °C (acetone/diethyl ether), colorless crystals, $[\alpha]_D^{22}$ = +30.8° (c = 1, CHCl$_3$), R_f = 0.43 (chloroform-methanol 9:1). – IR (KBr): ν/cm^{-1} = 3185, 3292, 3358, 3394 (NH$_2$, OH), 1672, 1631 (C=O, NH$_2$), 1584, 1543 (C=C). – ^{1}H NMR (300 MHz, CDCl$_3$): δ/ppm = 2.57 (d, 1H, ^3J = 5.3 Hz, OH), 3.65 (m, 3H, $^3J_{2',1'}$ = 6.1 Hz, 3'ab-H, 2'-H), 4.27 (d, 1H, ^2J = 11.8 Hz, 1CHHPh), 4.31–4.40 (m, 2H, 2CHHPh), 4.46 (d, 1H, 1CHHPh), 4.55 (dd, 1H, 1CHHPh), 4.62 (d, 1H, ^2J = 11.4 Hz, 1CHHPh), 4.82 (d, 1H, 1'-H), 5.60 (s, 2H, NH$_2$), 6.55 (s, 2H, CONH$_2$), 6.98–7.40 (Ph), 7.71 (s, 1H, 4-H). – ^{13}C NMR (300 MHz, CDCl$_3$): δ/ppm = 62.0, 71.2, 71.9, 73.1, 73.4 (5CH$_2$), 76.4 (C-1'), 82.0 (C-2'), 108.7 (C-3), 121.2 (C-5), 128.2–138.3 (Ph), 137.5 (C-4), 158.2 (C-6), 159.2 (C-2), 170.1 (C=O). – MS (CI-Isobutane): m/e (%) = 528 (29) (MH$^+$), 420 (18) (M – OCH$_2$Ph).
C$_{31}$H$_{33}$N$_3$O$_5$ calcd: C 70.50 H 6.25 N 7.96
(527.62)   found: C 70.38 H 6.52 N 7.93.

Ring Transformation with Cyanoacetamide

5-(1,2,4-Tri-O-benzyl-D-arabino-1,2,3,4-tetrahydroxy-butyl)-1,2-dihydro-2-oxo-pyridine-3-carbonitrile (**12a**)

0.5 g (6.0 mmol) cyanoacetamide was suspended in a solution of **2a** (1.33 g, 3.0 mmol) in toluene (20 ml). Acetic acid (0.1 ml, 1.7 mmol) and piperidine (0.05 ml, 0.51 mmol) were added, and the mixture was heated under reflux with a Dean-Stark trap for 3h. After removal of the solvent the resulting crude syrup was purified by elution from a silica gel column

(20 cm) with chloroform-methanol 9 : 1 to afford 0.84 g (48.5%) of **12a**, *m.p.* 146 °C (acetone/diethyl ether), $[\alpha]_D^{22} = -65.4°$ (c = 1, CHCl$_3$), R_f = 0.57 (chloroform-methanol 9:1). - IR (nujol): v/cm^{-1} = 3189, 3346, 3473 (NH, OH),), 2224 (CN), 1651 (C=O). - ^{1}H NMR (300 MHz, [D$_6$] DMSO): δ/ppm = 3.50 (m, 2H, $^2J_{4a',4b'}$ = 10.68 Hz, $^3J_{2',1'}$ = 3.05 Hz, 4'a-H, 2'-H,), 3.64 (dd, 1H, 4'b-H), 3.85 (m, 1H, 3'-H), 4.19 (d, 1H, ^2J = 11.06 Hz, 1CHHPh), 4.35 (dd, 2H, 2CHHPh), 4.48 (m, 3H, 3CHHPh), 4.61 (d, 1H, 1'-H), 4.98 (s, 1H, 3'-OH), 7.04–7.40 (Ph), 7.64 (d, 1H, $^4J_{4,6}$ = 2.44 Hz, 4-H), 7.99 (d, 1H, 6-H), 12.45 (s,1H, 2-OH). – ^{13}C NMR (300 MHz, [D$_6$] DMSO): δ/ppm = 70.6 (C-2'), 71.8, 72.8, 73.6, 75.1 (C-4', 3CH$_2$Ph), 78.0 (C-1'), 83.7 (C-3'), 104.2 (C-3), 116.2 (CN), 116.8 C-4), 127.9–137.8 (Ph), 141.1 (C-3), 149.8 (C-5), 160.9 (C=O). –MS (CI-Isobutane): *m/e* (%) = 511 (48) (MH$^+$). C$_{31}$H$_{31}$N$_3$O$_4$ calcd: C 72.92 H 5.92 N 5.49 (510.59) found: C 72.82 H 5.98 N 5.43.

5-(1,2,4-Tri-O-benzyl-D-lyxo-1,2,3,4-tetrahydroxy-butyl)-1,2-dihydro-2-oxo-pyridine-3-carbonitrile (**12b**)

2b (1.33 g, 3.0 mmol) was treated with cyanoacetamide (0.5 g, 6.0 mmol), as described for preparation of **12a**. Yield 1.07 g (62.5%), *m.p.* 154–156 °C (acetone/diethyl ether), $[\alpha]_D^{22} = -10.87°$ (c = 1, CHCl$_3$), R_f = 0.58 (chloroform-methanol 9:1). - IR (KBr): v/cm^{-1} = 3274, 3291, 3338 (NH, OH), 2226 (CN), 1657 (C=O). - ^{1}H NMR (300 MHz, [D$_6$] DMSO): δ/ppm = 3.49 (m, 2H, $^3J_{4a',3'}$ = 6.49 Hz, 4'a,b-H), 3.67 (dd, 1H, $^3J_{2',1'}$ = 7.63 Hz, $^3J_{2',3'}$ = 5.34 Hz, 2'-H), 4.00 (m, 1H, 3'-H), 4.16 (d, 1H, ^2J = 10.99 Hz, 1CHHPh), 4.33–4.54 (m, 6H, 1'-H, 5CHHPh), 4.74 (s, 1H, ^3J = 6.48 Hz, 3'-OH), 7.00–7.38 (m, 16H, Ph), 7.68 (d, 1H, $^3J_{4,6}$ = 2.44 Hz, 4-H), 8.08 (d, 1H, 6-H), 12.44 (s, 1H, 2-OH). – ^{13}C NMR (300 MHz, [D$_6$] DMSO): δ/ppm = 68.3 (C-2'), 70.1, 71.0, 72.3, 73.7 (C-4', 3CH$_2$Ph), 76.5 (C-1'), 80.6 (C-3'), 103.0 (C-3), 116.2 (CN), 116.8 (C-5), 127.5–138.5 (Ph), 140.5 (C-4), 148.5 (C-6), 159.7 (C-2). – MS (CI-Isobutane): *m/e* (%) = 511 (60) (MH$^+$). C$_{31}$H$_{30}$N$_2$O$_5$ calcd: C 72.92 H 5.92 N 5.49 (510.59) found: C 72.83 H 6.18 N 5.52.

References

[1] L. I. Haynes, Adv. Carbohydr. Chem. **1963**, *18*, 227

[2] L. I. Haynes, Adv. Carbohydr. Chem. **1965**, *20*, 357

[3] H. J. Schaeffer, L. Beauchamp, P. de Miranda, G. B. Elion, D. J. Bauer, P. Collins, Nature (London) **1978**, *272*, 583

[4] C. K. Chu and S. J. Cutler, J. Heterocyclic Chem. **1986**, *23*, 289

[5] R. J. Remy, J. A. Secrist, Nucleosides & Nucleotides **1985**, *4*, 411

[6] M. Valpuesta Fernández, F. J. López Herrera, C. Gómez Pérez, Carbohydr. Res. **1983**, *124*, 333

[7] M. Mancera, E. Rodriguez, I. Roffé, J. A. Galbis, C. F. Conde, A. Conde, Carbohydr. Res. **1991**, *210*, 327

[8] M. Mancera, E. Rodriguez, I. Roffé, J. A. Galbis, Carbohydr. Res. **1994**, *253*, 307

[9] J. C. Bernal Montes, P. Borrachero Moya, F. Cabrera Escribano, M. Gómez Guillén, F. Madrid Díaz, J. M. Moreno Martínez, Carbohydr. Res. **1996**, *285*, 49

[10] A. Zamojski, A. Banaszek, G. Grynkiewicz, Adv. Carbohydr. Chem. Biochem. **1982**, *40*, 1

[11] U. Nubbemeyer, Synthesis **1993**, 1120

[12] P. François, D Perilleux, Y. Kempener, E. Souveaux, Tetrahedron Lett. **1990**, *31*, 6347

[13] R. Csuk, A. Fürstner, H. Weidemann, J. Chem. Soc., Chem. Comm. **1986**, 775

[14] J.-A. Mahling, R. R. Schmidt, Synthesis **1993**, 325

[15] H. Togo, M. Fujii, T. Ikuma, M. Yokoyama, Tetrahedron Lett. **1991**, *32*, 3377

[16] K. Peseke, H. Feist, E. Cuny, Carbohydr. Res. **1992**, *230*, 319

[17] K. Peseke, G. Thiele, M. Michalik, Liebigs Ann. **1995**, 1633

[18] H. Junjappa, H. Ila, C. V. Asokan, Tetrahedron **1990**, *46*, 5423

[19] M. Kolb, Synthesis **1990**, 171

[20] R. K. Dieter, Tetrahedron **1986**, *42*, 3029

[21] N. G. Ramesh, K. K. Balasubramanian, Tetrahedron Lett. **1991**, *32*, 3875

[22] W. Roth, W. Pigman, Methods Carbohydrate Chem. **1963**, *2*, 407

[23] N. V. Bovin, S. Zurabyan, Carbohydrate Res. **1981**, *98*, 25

[24] F. W. Lichtenthaler, S. Hahn, F.-J. Flath, Liebigs Ann. Chem. **1995**, 2081

[25] N. Bovin, S. Zurabyan, J. Carbohydr. Chem. **1983**, 249

[26] Organikum, Johann Ambrosius Barth Verlag, Heidelberg, Leipzig 1996, p. 502

[27] K. Peseke, Z. Chem. **1977**, *17*, 288

[28] G. Ege, H. O. Frey, E. Schuck, Synthesis **1979**, 376

[29] W. Kantlehner, I. C. Ivanov, W. W. Mergen, H. Bredereck, Liebigs Ann. Chem. **1980**, 372

Address for correspondence:
Prof. Dr. K. Peseke
Fachbereich Chemie
Universität Rostock
Buchbinderstr. 9
D-18051 Rostock