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Synthesis and Structural Studies of Asparagine-Modified 2-Deoxy-α-*N*-Glycopeptides Associated with the Renin–Angiotensin System

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Abstract—Following addition of N-iodosuccinimide to glycals, reductive hydrogenolysis and ring opening gave 2-deoxy-α-N-glycopeptides carrying a deaminated asparagine unit. This reaction could be performed employing glucal, galactal, L-rhamnal, L-fucal and lactal to give the corresponding glycoconjugate building blocks **11**, **12**, **17**, **22**, **27** and **32**. Further NIS-mediated glycosylation of the rhamno derivative **21** led to simple trisaccharide peptide adducts **45**. Peptide synthesis of the gluco building unit with different preassembled oligopeptides afforded glycoconjugates **36**, **39**, **41** and **42** assumed to be of interest as potential inhibitors of the renin–angiotensin system.

Introduction

It is well established that the majority of naturally occurring proteins are found as glycoconjugates and it is accepted that most of the post translational biological selectivity is based on glycoprotein recognition.[1–3] Glycosylation of proteins at distinct asparagine, serine or threonine residues modifies the physical characteristics of the protein including tertiary structure, protein folding and stability. This is also believed to alter the functional characteristics of proteins such as enzymes. Thus, the protein–substrate recognition phenomena in some cases are proven to occur at the carbohydrate site of the glycoprotein.[4]

To this aspect Ashwell *et al.* first proved the role carbohydrate moieties contribute to substrate recognition.[5] When one neuraminic acid residue was cleaved from the oligosaccharide part of coeruloplasmine the half life in rabbit serum was reduced more than 600 times. Further, when regular formation of glycoconjugates on the surface of the cell wall was prevented, cell growth was considerably affected.[6] This is in accordance with the observation that tumour cells are associated with carbohydrate antigens which do not occur in non-pathogen cells.[7] Even viral or bacterial infections may be guided by the carbohydrate pattern of the host cell.[8]

On the other hand, recognition phenomena mediated by sugar residues may be exploited for specific drug targeting. Biologically active synthetic proteins or peptides may be addressed to a specific receptor by the appropriate glycosylation pattern. Bearing in mind that proteolytic enzymes are much less effective on glycosylated peptides,[9,10] the biological stability and consequently the availability of the peptide is enhanced. Thus, concepts for the synthesis of orally applicable and pharmaceutically active peptides is of prime interest.

The synthesis of N-glycopeptides is still an exciting issue in natural product synthesis and it has been addressed increasingly in the last decade.[11–13] Whereas previous efforts have successfully focused on β-N-glycosidically linked asparagine as the central structural unit of natural N-linked glycopeptides, the α-linked N-glycoconjugates have drawn comparatively little interest. The isolation of the first naturally occurring and biologically active α-N-glycoprotein, as an exception to the rule, by Shibata *et al.*[14,15] prompted some synthetic efforts towards these targets. Recently Shibata *et al.*[16] synthesised a part of the glycopeptide nephritogenoside consisting of 21 amino acids which are α-N-linked via their N-terminal asparagine unit to three α,1–6-linked glucose units. Using their *n*-pentenyl glycoside protocol Fraser-Reid *et al.* were the first to come up with a straightforward synthesis of these crucial α-N-linked glycopyranosyl amides.[17] This method avoids the major set-back in the previous syntheses[16] arising from anomerisation of the intermediate glycosyl amine derived from glycosyl azide. Since amidases cleave the N-glycosidic bond in glycopeptides with little regard to both the carbohydrate and the peptide pattern,[12,18,19] the goal of our work was to find suitable modifications. In particular the close surrounding of the glycosidic linkage was intended to be varied which should prevent an amidase such as L-asparagine-hydrolase [E.C. 3.2.2.11] from cleaving.[20] Thus the introduction of the 'wrong' α-anomeric linkage as well as 2-deoxygenation of the N-linked sugar was attempted. This idea is supported by results obtained with 2-deoxy oligosaccharides of various pharmaceuticals such as anthracyclines.[21] Further, the lack of the 2-amino function of the glycosidically attached asparagine seems to be advantageous since it is essential for enzymatic activity of L-asparagine-hydrolase.[12,18,19]

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Previously compound **4** could be obtained in the N-iodosuccinimide (NIS) glycosylation procedure as a side product. In the light of these results this reaction was reinvestigated, and here we wish to report a new strategy for the synthesis of asparagine-modified 2-deoxy-α-N-glycopeptides and its application to some peptide components designed as inhibitors for the renin–angiotensin system (RAS).

Strategic Approach

N-Iodosuccinimide (NIS) has proven to be an effective reagent for the stereoselective glycosylation of glycals. Whenever alcohols of lower nucleophilicity were submitted to this glycosylation procedure[22,23] it was observed that the succinimide anion was competing with the aglyconic nucleophile in the attack of the intermediary iodonium cation.

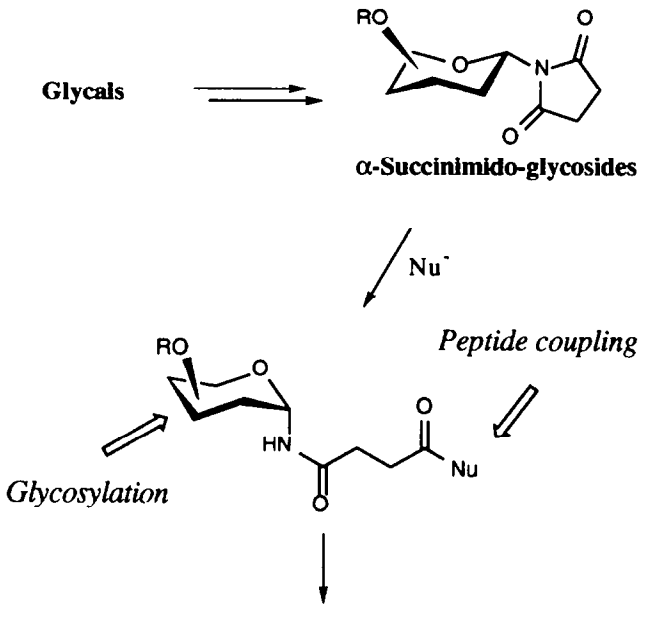
In the absence of other nucleophiles and exclusion of light a completely stereoselective addition of NIS is observed in high to excellent yields. Benzyl or acetyl protected glycals which are readily available mono- and disaccharide building blocks were submitted to this procedure.

Following dehalogenation of the 2-iodo substituent the imide ring can be easily opened with nucleophiles to yield an α-N-glycosyl amide (Scheme I). These compounds are stable and may be stored in the freezer for years. The monosaccharide moiety can be readily further glycosylated employing various protecting groups which can be easily removed. The nucleophile used to open the imide determines the protection of the carboxylic acid. The free acid or its derivatives in turn can be submitted to a coupling procedure with preassembled peptides. These considerations made the 2-deoxy glycosyl amides a central building block in our work towards α-N-glycopeptides.

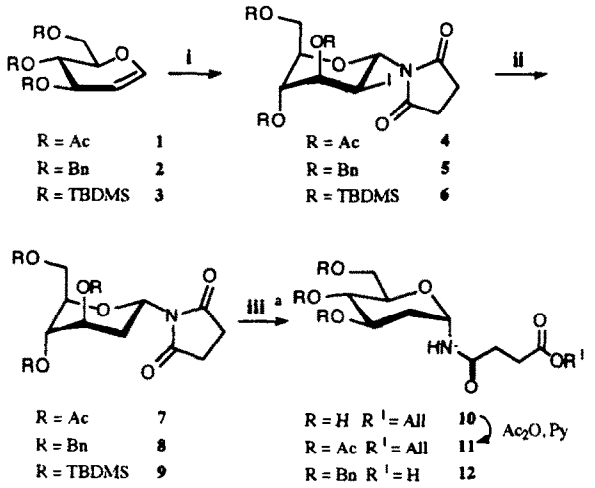
The reaction sequences starting from variously blocked glycals are outlined in detail in Schemes II and III. Compounds **11**, **12** and **22** were synthesized in excellent overall yield of 83 %, 88 % or 80 % respectively. Often for convenience the crude products were used, e.g. this is a quick access from crude **5** and **8** to compound **12**. In the D-galacto- (**13** → **17**) and L-fuco- (**23** → **27**) series overall yields of 51 % and 26 % were obtained due to side reactions. Less reactive glycals such as lactal **28** showed slow reaction rates, and a considerable amount of iodine was liberated. This caused side reactions which lowered the yield of **29** to 45 %; nevertheless, the overall yield of **32** was still 31 %. In order to demonstrate the flexibility of the approach the deblocked rhamnosyl amide **21** was chosen for further glycosylation and the gluco derivative **12** for further peptide couplings.

Peptide Coupling

The peptides depicted in Scheme IV were synthesized as potential inhibitors of the renin–angiotensin system.[24] In medicinal chemistry an active therapeutic agent for the treatment of hypertension and conjectural heart failure which could be orally applied remains a challenging target.[25] Peptide analogues of the angiotensin region flanking the bond cleaved by renin have proven to be powerful inhibitors of the renin–angiotensin system. Especially ACHPA [(3*S*,4*S*)-4-amino-5-cyclohexyl-3-hydroxy-pentanoic acid] containing peptides have drawn much attention. In order to become a viable drug an orally active renin inhibitor has to be absorbed within the gastrointestinal tract into the systemic circulation in order to reduce the blood pressure when given orally. Several approaches have been undertaken focusing mainly on the

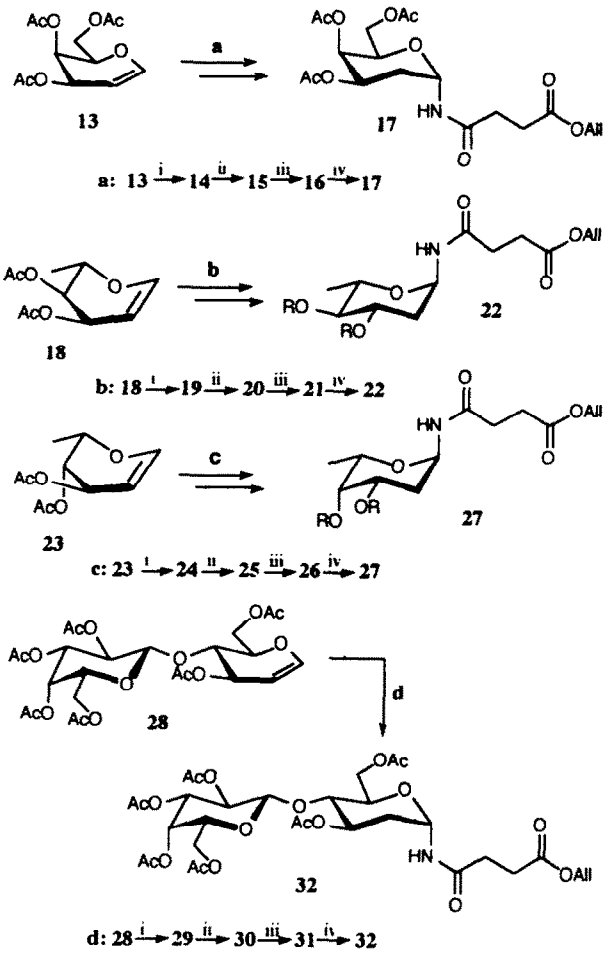


Scheme I.



i: NIS, CH_3CN, 24 h, rt. ii: n-Bu_3SnH, Toluene, AIBN, 80 °C. iii: Allyl-OH, Allyl-ONa, rt. iv: Ac_2O, Py, 4 h, rt. a) Conditions used for 8→12: THF/H_2O 2:1, KOH.

Scheme II.



For reaction conditions i–iv refer to Scheme II.

Scheme III.

variation of the peptide chain.[26] We herein describe our synthetic efforts towards a glycosylated renin inhibitor as a new approach to this problem.

The reaction conditions for coupling the oligopeptide to the glycosyl amides have to be chosen very carefully.[12,13] In our hands EEDQ, Et_3N in CH_2Cl_2 worked most efficiently with yields from 60 to 75 %, and in HPLC-analysis no trace of any diastereomer was observed. The benzyl groups were readily removed by hydrogenolysis with Pd/C in methanol to give yields above 90 %.

Glycosylation

The 3,4-deblocked rhamnosyl amide **21** and lactal **28** were submitted to an NIS glycosylation procedure.[21] No formation of the bis-glycosylated derivative was observed, but in a regioselective mode α,1→3 derivative **43** and its α,1→4 regioisomer (not depicted in Scheme IV) were synthesised in a 4:1 ratio. The isomers were separated on a silica gel column to yield **43** (40 %) and the regioisomer (10 %). The remaining free hydroxy group of **43** was acetylated in 71 %, and according to Kunz *et al.*[27] the allyl ester was liberated with $Pd(PPh_3)_4$, morpholine in THF to give the deblocked trisaccharide asparagine mimic. Valine could be attached to the free acid as above to yield 67 % of **45**.

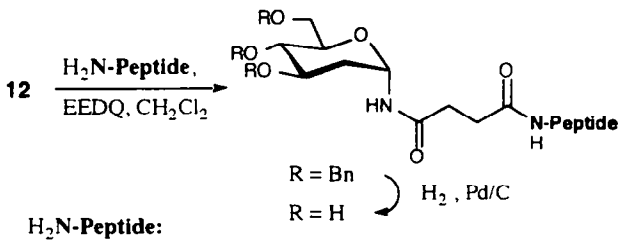
In conclusion an efficient and high yielding approach to an anomerically pure mimicry of natural N-glycopeptides could be demonstrated. The modifications at the linkage between asparagine and the carbohydrate units is thought to ensure a slower degradation of these glycopeptides.

Since the oligopeptides and oligosaccharides can be constructed separately the range of applications should be rather broad. Tests for biological properties of the compounds described as renin inhibitors are presently done elsewhere and further syntheses of higher oligosaccharide- and peptide-conjugates are currently being studied in our laboratory.

Conformational Analysis

En route to the glycopeptides various NIS-adducts and their dehalogenated derivatives were synthesized (Schemes II and III) and the NMR data showed interesting conformational features. At first sight, one is inclined to attribute a reverse anomeric effect to the imide at C-1, since the protected glycosyl imides show considerable up to complete amounts of the 'inverse' $^1C_4$ (D) or $^4C_1$ (L) chair conformation. The conformational equilibria were estimated using the *trans*-$J_{4,5}$ and the *trans*-$J_{1,2}$ coupling constants.[28–30] With regard to both constants in the synthesized succinimido-series the boat form was very unlikely. However, only for the galacto derivative no decision could be made based on the available data.

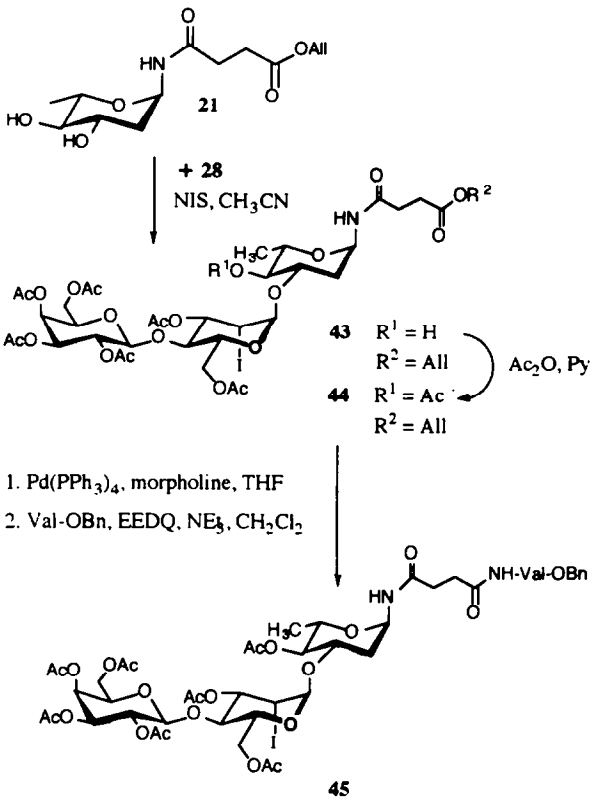
The $^1C_4$ (D)-form has to be clearly postulated for all gluco-compounds with the 2-deoxy-2-iodo function due to the large *trans*-$J_{1,2}$ (> 10 Hz) and small $J_{4,5}$ (< 2.8 Hz) coupling constants. With regard to the halogenated compounds this effect can apparently be attributed to the iodine substituent which owing to its large size forces all substituents at positions 3,4 and 6 into an axial position. For the dehalogenated glycosyl imides the situation is somewhat more complex because the conformational mixtures ranging from 100 % $^1C_4$ to about 100 % $^4C_1$ are observed depending solely on the choice of protecting groups at 3-,4- and 6-positions. Attachment of a 4,6-*O*-isopropylidene group leads to the expected $^4C_1$ chair exclusively, and for the deblocked imide **46** this 'normal' conformation is estimated to predominate ($^4C_1$:$^1C_4$ = 4:1). Increasing the steric demands of the 3,4,6-substituents in line with benzyl-, acetyl-, TMS- and TBDMS-protected derivatives (**8**, **7**, **48** and **9**) the conformation is changing to a preferred $^1C_4$ chair form (Table 1).



H_2N-Peptide:	
H-Leu-OAll	**33** R = Bn → **34** R = H
H-Ser-Phe-Leu-OPropyl	**35** R = Bn → **36** R = H
	37[a] R = Ac
H-Ser-ACHPA-Ile-OMe	**38** R = Bn → **39** R = H
H-Ser-Leu-ACHPA-Ile-OMe	**40** R = Bn → **41** R = H
H-Ser-Phe-Leu-ACHPA-Ile-OMe	**42** R = Bn

a: Precusor **11**, deblocked using $Pd(PPh_3)_4$, morpholine in THF AHCP = 3*S*,4*S*-4- Amino-5-cyclohexyl-3-hydoxy-pentanoic-acid.

Scheme IV.



Scheme V.

Table 1.

Compounds	trans-$J_{1,2}$	$J_{4,5}$	$^1C_4$	$^4C_1$
4	10.5	2.8	>9	1
5	10.5	2.5	>9	1
6	10.5.	2.0	10	0
47 (4,6-O-isoprop)	1.0	10.5	0	10
46 (OH)	3.0	9.0	2	8
8 (OBn)	7.0	7.0	5	5
7 (OAc)	7.0	7.0	5	5
48 (OTMS)	7.0	6.0	6	4
9 (OTBDMS)	11.0	2.0	10	0

In conclusion the imide shows a rather 'normal' anomeric effect, but the observed conformation is strongly dependent on the 3-, 4- and 6-substituents. Obviously these interactions are minimized, e.g. in the gluco-series, with all substituents in the unexpected axial position.

Experimental

General

Reactions were followed by TLC on silica gel foils (Merck, silica gel 60, GF254). Detection was by UV and spraying with 10 % ethanolic sulfuric acid with subsequent heating to 150 °C. Column chromatography was carried out on silica gel (230–400 mesh) with the solvents indicated using the flash technique. Melting points were taken on a Reichert heating microscope or an Olympus polarizing microscope and are uncorrected. Optical rotations were measured with Perkin–Elmer polarimeters 241 or 243 in 1 dm cuvettes at 589 nm. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AC-250 (^1H: 100 MHz, ^{13}C: 62.89 MHz), WM-400 and AMX-400 (^1H: 400 MHz, ^{13}C: 100.67 MHz) with TMS or $CDCl_3$ as internal standards. For NMR data of oligosaccharides the non-reducing sugars were denominated as A-ring, the subsequent ones towards the terminal end as B- and C-rings. Syntheses were carried out under nitrogen with strict exclusion of moisture, and iodonium-catalysed reactions also under protection from light.

*N-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-iodo-α-D-mannopyranosyl)-succinimide (4)*

Under nitrogen 3,4,6-tri-*O*-acetyl-D-glucal (**1**) (2.72 g, 10.0 mmol) in anhydrous acetonitrile (15 mL) was treated with N-iodosuccinimide (NIS, 3.36 g, 15.0 mmol) at room temperature for 24 h. The reaction was followed by TLC, and after termination the solvent evaporated under reduced pressure. The residue was taken up in $CHCl_3$, washed three times with 10 % aqueous sodium thiosulfate solution, once with water and dried ($MgSO_4$). After evaporation the raw material was purified by flash chromatography (hexane:ethyl acetate, 1:1) to give **4** as a colourless material (4.57 g, 92 %); for physical data refer to Ref. 22.

*N-(3,4,6-Tri-*O*-benzyl-2-deoxy-2-iodo-α-D-mannopyranosyl)-succinimide (5)*

Following the protocol for the synthesis of **4**, 3,4,6-tri-*O*-benzyl-D-glucal (**2**, 4.09 g, 10.0 mmol) was treated with NIS (2.24, 10.0 mmol) worked up and purified by flash chromatography (toluene:ethyl acetate, 5:1) to give **5** as a syrup (5.84 mg, 95 %); $[\alpha]_D^{20} = 3.0$ ° (c = 1.0, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): δ = 5.80 (d, H-1), 5.70 (dd, H-2), 3.92 (dd, H-3), 3.57 (dd, H-4), 4.50 (mc, H-5), 3.68 (dd, H-6), 3.81 (dd, H-6'), 7.30–7.50 (m, 15H, aryl-H), 4.40–4.60 (m, 6-H, 3 CH_2-Ph), 2.62 (s, 4H, CH_2-imide); $J_{1,2} = 10.4$, $J_{2,3} = 2.8$, $J_{3,4} = 2.8$, $J_{4,5} = 2.8$, $J_{5,6} = 5.8$, $J_{5,6'} = 6.8$, $J_{6,6'} = 12.0$ Hz. ^{13}C NMR ($CDCl_3$): δ = 79.14 (C-1), 25.93 (C-2), 75.56, 72.95 (C-3, C-4), 76.41 (C-5), 67.75 (C-6), 27.93 (CH_2-imide), 73.55, 73.34, 72.95 (3 CH_2-Ph), 176.15 (s, 2 C=O imide), 138.2–127.48 (C-aryl).

*N-(2-Deoxy-3,4,6-tri-*O*-tert-butyldimethylsilyl-2-iodo-α-D-mannopyranosyl)-succinimide (6)*

Following the protocol for the synthesis of **4**, compound **3** (Ref. 31) (552 mg, 1.13 mmol) was treated with NIS, worked up and purified by flash chromatography (petroleum ether:diethyl ether, 3:1) to give **6** as a white solid material (493 mg, 84 %); mp 108 °C; $[\alpha]_D^{20} = +43$ ° (c = 0.51, $CHCl_3$); ^1H NMR ($CDCl_3$):δ = 5.68 (d, H-1), 5.79 (dd, H-2), 4.06–4.11 (m, 2H, H-3, H-6), 3.90 (dd, H-4), 3.96 (dd, H-5), 3.84 (dd, H-6), 2.69 (s, 4H, imide), 0.04–0.23 (m, 18H, Si-CH_3), 0.87–0.99 (m, 27H, Si-^{t}Bu); $J_{1,2} = 10.5$, $J_{2,3} = 2.0$, $J_{3,4} = 1.5$, $J_{4,5} = 2.0$, $J_{5,6} = 6.0$, $J_{5,6'} = 8.0$, $J_{6,6'} = 10.0$ Hz. ^{13}C NMR ($CDCl_3$): –5.34– –3.64 (6C, Si-CH_3), 17.86, 18.21, 18.25 (3C, Si-C), 25.65–26.37 (9C, Si-^{t}Bu-CH_3), 27.85 (2C, imide), 29.16 (C-2), 60.96 (C-6), 68.86 (C-3), 74.02, 75.60 (2C, C-4, C-5), 81.55 (C-1), 175.8 (2C, C=O). Calcd for $C_{28}H_{56}INO_6Si_3$ (713.9): C, 47.11; H, 7.91; found: C, 47.05; H, 7.95.

*N-(3,4,6-Tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-succinimide (7)*

Compound **4** (2.49 g, 5.0 mmol) was dissolved in anhydrous toluene (10 mL) under argon cover and treated with tri-*n*-butyl stannic hydride (2.0 mL, 7.5 mmol). A catalytic amount of azobisisobutyronitrile was added and the mixture heated to 80 °C for 5 h. Following evaporation of the solvent the residue was taken up in acetonitrile and the stannic compounds extracted several times with hexane. The residue was purified by flash chromatography (hexane:ethyl acetate, 1:1) to give **7** as a colourless solid material (1.76 g, 95 %); mp 132 °C; $[\alpha]_D^{20} = +39.0$ ° (c = 1.0, $CHCl_3$); ^1H NMR (C_6D_6): δ = 5.96 (dd, H-1), 2.83 (ddd, H-2), 1.80 (dt, H-2'), 5.74 (m, H-3), 5.22 (dd, H-4), 4.56 (ddd, H-5), 4.32 (dd, H-6), 4.46 (dd, H-6'), 1.57 (s, 4H, imide), 1.95–2.05 (3s, 9H, 3 OAc); $J_{1,2} = 7.0$, $J_{1,2'} = 5.8$, $J_{2,2'} = 14.0$, $J_{2,3} = 5.0$, $J_{2',3} = 5.8$, $J_{3,4} = 5.2$, $J_{4,5} = 7.0$, $J_{5,6} = 3.0$, $J_{5,6'} = 5.4$, $J_{6,6'} = 12.0$ Hz. ^{13}C NMR ($CDCl_3$): δ = 73.05, 72.57, 70.13, 68.52 (C-1, C-3, C-4, C-5), 28.46 (C-2), 61.95 (C-6), 28.12 (2 C-imide), 176.69 (s, 2 C=O-imide), 170.67, 169.83, 169.67 (3 C=O acetyl), 21.00, 20.82, 20.74 (3 CH_3-acetyl). Calcd for $C_{16}H_{21}NO_9$ (371.4): C, 51.75; H, 5.70; N, 3.77; found: C, 51.24; H, 5.71; N, 3.71.

*N-(3,4,6-Tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-succinimide (8).*

Following the protocol for the synthesis of **7**, compound **5** (3.17 g, 5 mmol), was treated with *n*-Bu_3SnH, worked up and purified by flash chromatography (toluene:ethyl acetate, 4:1) to give **8** as a syrup (2.42 mg, 94 %); $[\alpha]_D^{20} = +27.5$ ° (c = 1.0, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): δ = 5.85 (dd, H-1), 2.87 (ddd, H-2), 1.96 (ddd, H-2'), 4.12 (dd, H-3), 3.61 (dd, H-4), 4.17 (mc, H-5), 3.66 (dd, H-6), 3.73 (dd, H-6'), 7.20–7.40 (m, 15 H, aryl-H), 4.46–4.63 (m, 6H, 3 CH_2-Ph), 2.62 (s, 4H, CH_2-imide); $J_{1,2} = 7.0$, $J_{1,2'} = 5.2$, $J_{2,2'} = 14.0$, $J_{2,3} = 4.0$, $J_{2',3} = 1.0$, $J_{3,4} = 4.0$, $J_{4,5} = 7.0$, $J_{5,6} = 3.4$, $J_{5,6'} = 5.0$, $J_{6,6'} = 10.8$ Hz. ^{13}C NMR ($CDCl_3$): δ = 76.20 (C-1), 28.18 (C-2), 74.92, 73.93 (C-3, C-4), 75.64 (C-5), 68.88 (C-6), 28.18 (CH_2-imide), 73.25, 73.53, 71.23 (3 CH_2-Ph), 176.74 (s, 2 C=O-imide), 138.2–127.48 (C-aryl). Calcd for $C_{31}H_{33}NO_6$ (515.6): C, 72.21; H, 6.45; N, 2.72; found: C, 71.22; H, 5.09; N, 2.66; (partial decomposition).

*N-[2-Deoxy-3,4,6-tri-*O*-tertbutyldimethylsilyl-α-D-*arabino*-hexopyranosyl]-succinimide (9)*

At –80 °C *tert*-butyldimethylsilyl-triflate (7.0 mL, 30.1 mmol) was added slowly to a solution of dry THF (50 mL), pyridine (20 mL) and of **46** (2.25 g, 9.23 mmol). The solution was slowly allowed to warm to room temperature and stirred overnight. Pyridine and THF were evaporated and the residue was taken up in ether (50 mL). The organic phase was washed with water (3 × 30 mL), $NaHCO_3$ solution (30 mL), and brine (30 mL), dried (Na_2SO_4) and concentrated. The crude oil was purified by flash chromatography on silica (toluene:ethyl acetate, 8:1) to yield 5.2 g (96 %) of **9** as a white solid; mp 98 °C; $[\alpha]_D^{20} = +5.0$ ° (c = 0.84, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 5.73 (dd, H-1), 3.25 (ddd, H-2), 1.40 (ddd, H-2'), 3.98–4.02 (m, 2H, H-3, H-6), 3.69 (dd, H-4), 3.92 (ddd, H-5), 3.85 (dd, H-6'), 2.65 (s, 4H, imide), 0.03–0.08 (m, 18H, Si-CH_3), 0.86–0.93 (m, 27H, ^{t}Bu-Si); $J_{1,2} = 11.0$, $J_{2,3} = 1.5$, $J_{1,2'} = 2.5$, $J_{3,4} = 2.5$, $J_{4,5} = 2.0$, $J_{5,6} = 6.0$, $J_{5,6'} = 6.5$, $J_{6,6'} = 10.0$ Hz. ^{13}C NMR ($CDCl_3$): –4.72 – –5.35 (6C, Si-CH_3),

25.14, 25.17, 25.29 (9C, ^{t}Bu-Si), 17.90, 17.97, 18.21 (3C, ^{t}Bu-Si), 28.05 (2C, imide), 29.25 (C-2), 61.45 (C-6), 67.58, 70.95, 71.45 (C-3, C-4, C-5), 81.36 (C-1), 176.34 (imide). Calcd for $C_{28}H_{56}INO_6Si_3$ (588.0): C, 57.19; H, 9.77; N, 2.38; found: C, 57.24; H, 9.76; N, 2.36.

*N-(2-Deoxy-α-D-*arabino*-hexopyranosyl)-succinamic acid allyl ester (10)*

Compound **7** (371 mg, 1.0 mmol) was dissolved in allyl alcohol (5 mL) and treated with freshly prepared sodium allylate until pH 10 was reached. After 3 h at room temperature the mixture was neutralized with Amberlite IR 120 H^+, filtered and evaporated. Purification by flash chromatography gave 10 as a colourless syrup (287 mg, 95 %); $[\alpha]_D^{20}$ = +102.0 ° (c = 1.0, CH_3OH); ^{1}H NMR (CD_3OD): δ = 5.53 (m, H-1), 1.81 (ddd, H-2), 1.97 (ddd, H-2'), 3.86 (ddd, H-3), 3.24 (dd≈t, H-4), 3.42 (ddd, H-5), 3.66 (dd, H-6), 3.74 (dd, H-6'), 2.57 and 2.65 (each m, each 2H, CH_2), 4.57 (d, 2H), 5.93 (m, allyl-Hβ), 5.32 and 5.22 (each dd, each 1H, allyl-Hτ); $J_{1,2}$ = 5.0; $J_{1,2'}$ = 1.2, $J_{2,2'}$ = 13.6, $J_{2,3}$ = 11.6, $J_{2',3}$ = 5.0, $J_{3,4}$ = 8.8, $J_{4,5}$ = 8.8, $J_{5,6}$ = 5.4, $J_{5,6'}$ = 2.4, $J_{6,6'}$ = 11.8, $J_{\beta,\tau\text{-}trans}$ = 16.8, $J_{\beta,\tau\text{-}cis}$ = 10.6, $J_{\tau,\tau\text{-}gem}$ = 6.0 Hz.

*N-(3,4,6-Tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-succinamic acid allyl ester (11)*

Compound **10** (1.43 g, 5.0 mmol) was dissolved in anhydrous pyridine (10 mL) and treated with acetic anhydride (7.1 mL, 75.0 mmol). After completion of acetylation the residue was evaporated and codistilled three times with toluene. The raw material was purified by flash chromatography (toluene:ethyl acetate, 2:1) to give 11 as a colourless syrup (1.97 g, 92 %), $[\alpha]_D^{20}$ = +6.0 ° (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 6.86 (d, NH), 5.75 (m, H-1), 2.00–2.20 (m, 2H, H-2, -2'), 5.17 (ddd, H-3), 5.02 (dd≈t, H-4), 3.92 (ddd, H-5), 4.06 (dd, H-6), 4.35 (dd, H-6'), 2.54 and 2.73 (each m, each 2H, CH_2) 1.98–2.05 (3s, 9H, 3 OAc), 4.60 (d, 2H, allyl-Hα), 5.92 (m, allyl-Hβ), 5.25 and 5.32 (each dd, each 1H, allyl-Hτ); $J_{1,NH}$ = 7.6, $J_{2,3}$ = 10.4, $J_{2',3}$ = 5.6, $J_{3,4}$ = 8.2, $J_{4,5}$ = 8.8, $J_{5,6}$ = 4.4, $J_{5,6'}$ = 2.8, $J_{6,6'}$ = 12.0, $J_{\beta,\tau\text{-}trans}$ = 17.2, $J_{\beta,\tau\text{-}cis}$ = 10.4, $J_{\tau,\tau\text{-}gem}$ = 5.6 Hz. ^{13}C NMR ($CDCl_3$): δ = 73.61, 69.26, 68.88, 68.87 (C-1, C-3, C-4, C-5), 29.22 (C-2), 62.09 (C-6), 33.28 (CH_2-amide), 30.88 (CH_2-ester), 131.94 (CH_β-allyl), 118.47 (CH_τ-allyl), 65.53 (CH_α-allyl), 169.64, 170.51, 178,87, 171.65, 172.77 (5 C=O), 20.68, 20.73, 20.76 (3 CH_3-acetyl). Calcd for $C_{19}H_{27}NO_{10}$ (429.4): C, 53.14; H, 6.34; N, 3.26; found: C, 53.50; H, 6.41; N, 3.27.

*N-(3,4,6-Tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-succinamic acid (12)*

Compound **8** (509 mg, 0.99 mmol) was dissolved in tetrahydrofuran:water (2:1, 10 mL) and treated with potassium hydroxide (200 mg) for 1 h at room temperature. After dilution with chloroform (50 mL) extraction was done with cold hydrochloric acid (0.5 N). The organic layer was washed with water, dried ($MgSO_4$), filtered and evaporated. Purification by flash chromatography (toluene:ethyl acetate, 3:1) gave **12** as colourless needles (525 mg, 99 %); mp 148 °C (crystallized from CCl_4); $[\alpha]_D^{20}$ = +57.0 ° (c = 1.0 $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 5.79 (ddd, H-1), 2.17 (ddd, H-2), 1.88 (ddd, H-2'), 3.97 (dd, H-3), 3.68 (mc, 4 H, H-4, H-5, H-6, H-6'), 7.40–7.60 (m, 15 H, aryl-H), 4.42–4.63 (m, 6H, 3 CH_2-Ph), 2.60 (mc, 2H, CH_2), 2.50 (mc, 2H, CH_2), $J_{1,NH}$ = 8.0, $J_{1,2}$ = 4.4, $J_{1,2'}$ = 2.0, $J_{2,2'}$ = 13.2, $J_{2',3}$ = 5.2, $J_{2,3}$ = 10.8, $J_{3,4}$ = 9.6 Hz. ^{13}C NMR ($CDCl_3$): δ = 77.61 (C-1), 28.48 (C-2), 75.76, 73.79, 72.01 (C-3, C-4, C-5), 68.64 (C-6), 33.49 (CH_2-amide), 30.65 (CH_2-COOH), 75.41, 73.49, 71.12 (3 CH_2-Ph), 176.11 (-COOH), 171.18 (-CONH-), 138.2–127.8 (aryl-C).Calcd for $C_{31}H_{35}NO_7$ (533.6): C, 69.78; H, 6.61; N, 2.62; found: C, 70.13; H, 5.90; N, 2.64.

*N-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-iodo-α-D-talopyranosyl)-succinimide (14)*

3,4,6-Tri-*O*-acetyl-D-galactal (**13**, 2.72 g, 10 mmol) was treated with NIS and worked up as in the protocol for the preparation of **4**. Purification by flash chromatography (toluene:ethyl acetate, 3:1) gave **14** as a colourless solid (4.37 g, 88 %); mp 92 °C; $[\alpha]_D^{20}$ = +12.0 ° (c = 1.0, $CHCl_3$); ^{1}H NMR (C_6D_6): δ = 6.02 (d, H-1), 5.58 (dd, H-2), 5.66 (dd, H-3), 5.23 (dd, H-4), 4.44 (ddd, H-5), 4.49 (dd, H-6), 4.90 (dd, H-6'), 1.95–2.10 (3s, 9H, 3 OAc), 1.70 (s, 4H, CH_2); $J_{1,2}$ = 10.5, $J_{2,3}$ = 2.5, $J_{3,4}$ = 3.0, $J_{4,5}$ = 6.5, $J_{5,6}$ = 2.5, $J_{5,6'}$ = 9.5, $J_{6,6'}$ = 13.0 Hz. ^{13}C NMR ($CDCl_3$): δ = 73.83, 73.82, 70.50, 66.35 (C-1, C-3, C-4, C-5), 21.33 (C-2), 59.49 (C-6), 27.85 (2 C-imide), 175.66 (s, 2 C=O-imide), 171.25, 169.17, 169,18 (3 C=O-acetyl), 20.98, 20.83, 20.56 (3 CH_3-acetyl). Calcd for $C_{16}H_{20}INO_9$ (497.2): C, 38.65; H, 4.05; N, 2.82; I, 25.52; found: C, 38.66; H, 4.07; N, 2.89; I, 25.99.

*N-(3,4,6-Tri-*O*-acetyl-2-deoxy-α-D-*lyxo*-hexopyranosyl)-succinimide (15)*

Compound **14** (2.49 g, 5.0 mmol) was reduced with *n*-Bu_3SnH and worked up as described for the preparation of **7**. Flash chromatography (toluene:ethyl acetate, 2:1) gave pure **15** as colourless material (1.67 g, 90 %); mp 62 °C; $[\alpha]_D^{20}$ = +40.0 ° (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 5.88 (dd, H-1), 2.23 (ddd, H-2), 2.44 (dt, H-2'), 5.78 (ddd, H-3), 5.37 (dd≈t, H-4), 4.12 (ddd, H-5), 4.26 (dd, H-6), 4.28 (dd, H-6'), 2.75 (s, 4H, CH_2), 1.95–2.05 (3s, 9H, OAc); $J_{1,2}$ = 6.4, $J_{1,2'}$ = 4.8, $J_{2,2'}$ = 14.0, $J_{2,3}$ = 9.2, $J_{2',3}$ = 4.8, $J_{3,4}$ = 3.2, $J_{4,5}$ = 3.2, $J_{5,6}$ = 2.8, $J_{5,6'}$ = 7.2, $J_{6,6'}$ = 11.6 Hz. ^{13}C NMR ($CDCl_3$): δ = 73.09, 72.05, 67.01, 66.12 (C-1, C-3, C-4, C-5), 28.12 (C-2), 66.34 (C-6), 28.04 (2 C-imide), 176.76 (s, 2 C=imide), 170.57, 169.97, 169.76 (3 C=O-acetyl), 20.93, 20.75, 20.68 (3 CH_3-acetyl). Calcd for $C_{16}H_{21}NO_9$ (371.4): C, 51.75; H, 5.70; N, 3.77; found: C, 51.55; H, 6.00; N, 3.78.

*N-(2-Deoxy-α-D-*lyxo*-hexopyranosyl)-succinamic acid allyl ester (16)*

Compound **15** (371 mg, 1.0 mmol) was reacted and worked up as given in the preparation of **10**. Purification

by flash chromatography gave **16** as colourless syrup (230 mg, 80 %); $[\alpha]_D^{20}$ = +102.0 ° (c = 1.0, $CHCl_3$); ^1H NMR (CD_3OD): δ = 5.67 (m, H-1), 1.75 (ddd, H-2), 2.20 (ddd, H-2'), 4.09 (ddd, H-3), 3.00-3.87 (m, 4H, H-4,-5,-6,-6'), 2.64 and 2.71 (m, 4H, CH_2), 4.62 (d, allyl-Hα), 6.01 (m, allyl-Hβ), 5.31 and 5.37 (each dd, each 1H, allyl-Hτ); $J_{1,2}$ = 0.2, $J_{1,2'}$ = 5.0, $J_{2,2'}$ = 13.5, $J_{2,3}$ = 5.0, $J_{2',3}$ = 12.0, $J_{3,4}$ = 3.0, $J_{\beta,\tau\text{-}trans}$ = 17.0, $J_{\beta,\tau\text{-}cis}$ = 10.5, $J_{\tau,\tau'\text{-}gem}$ = 5.6 Hz. Calcd for $C_{13}H_{21}NO_7$ (303.3): C, 51.48; H, 6.98; N, 4.62; found: C, 54.60; H, 7.80; N, 4.90.

*N-(3,4,6-Tri-*O*-acetyl-2-deoxy-α-D-*lyxo*-hexopyranosyl)-succinamic acid allyl ester (17)*

Compound **16** (1.5 g, 5.51 mmol) was acetylated and worked up as described for the preparation of **11**. Purification by flash chromatography (toluene:acetone, 3:1) gave **17** as a syrup (172 mg, 81 %); $[\alpha]_D^{20}$ = +123.0 ° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 6.86 (d, NH), 5.71 (ddd, H-1), 2.00–2.20 (m, 2H, H-2, -2'), 4.99 (ddd, H-3), 5.38 (dd, H-4), 3.91 (ddd, H-5), 4.09 (dd, H-6), 4.17 (dd, H-6'), 1.98–2.05 (3s, 9H, 3 OAc), 2.52 and 2.72 (each m, each 2H, CH_2), 4.60 (d, allyl-Hα), 5.91 (m, allyl-Hβ), 5.23 and 5.32 (each dd, each 1H, allyl-Hτ); $J_{1,NH}$ = 7.8, $J_{2,3}$ = 5.6, $J_{2',3}$ = 10.2, $J_{3,4}$ = 3.6, $J_{4,5}$ = 0.4, $J_{5,6}$ = 7.2, $J_{5,6'}$ = 6.0, $J_{6,6'}$ = 11.4, $J_{\beta,\tau\text{-}trans}$ = 17.2, $J_{\beta,\tau\text{-}cis}$ = 10.4, $J_{\tau,\tau'\text{-}gem}$ = 5.6 Hz. ^{13}C NMR ($CDCl_3$): δ = 76.10, 72.65, 68.71, 65.49 (C-1, C-3, C-4, C-5), 29.03 (C-2), 65.47 (C-6), 31.49 (CH_2-amide), 30.85 (CH_2-ester), 131.93 (CH-allyl), 61.73 (CH_2-allyl), 172.50 (C=O-amide), 170.91, 170.50, 170.11, 169.82 (5 C=O-ester), 20.7–20.5 (3 CH_3-acetyl). Calcd for $C_{19}H_{27}NO_{10}$ (429.4): C, 53.14; H, 6.34; N, 3.26; found: C, 53.55; H, 6.41; N, 3.26.

*N-(3,4-Di-*O*-acetyl-2-deoxy-2-iodo-α-L-rhamnopyranosyl)-succinimide (19)*

3,4-Di-O-acetyl-L-rhamnal (**18**, 2.14 g, 10.0 mmol) was treated with NIS and worked up as in protocol for **4**. Purification by flash chromatography (toluene:ethyl acetate, 3:1) gave **19** as colourless needles (4.17 g, 95 %); for physical data refer to Ref. 22.

*N-(3,4,6-Tri-*O*-acetyl-2-deoxy-α-L-*arabino*-hexopyranosyl)-succinimide (20)*

Compound **19** (2.20 g, 5.0 mmol) was reduced with *n*-Bu_3SnH and worked up as given for **7**. Purification by flash chromatography gave colourless needles (1.41 g, 90 %); mp 197 °C; $[\alpha]_D^{20}$ = −22.0 ° (c = 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 5.78 (dd, H-1), 2.90 (ddd, H-2), 1.96 (dt, H-2'), 5.44 (ddd, H-3), 4.72 (dd, H-4), 4.13 (dq, H-5), 1.25 (d, 3H, H-6), 2.70 (s, 4H, CH_2), 1.98–2.20 (2s, 6H, 2 OAc); $J_{1,2}$ = 7.6, $J_{1,2'}$ = 5.6, $J_{2,2'}$ = 14.4, $J_{2,3}$ = 4.8, $J_{2',3}$ = 5.6, $J_{3,4}$ = 5.2, $J_{4,5}$ = 7.2, $J_{5,6}$ = 6.4 Hz. ^{13}C NMR ($CDCl_3$): δ = 73.09, 72.65, 70.75, 70.34 (C-1, C-3, C-4, C-5), 28.72 (C-2), 17.34 (C-6), 28.15 (2 C-imide), 176.86 (s, C=O-imide), 170.00, 169.90 (2 C=O-acetyl), 21.08, 20.97 (2 CH_3-acetyl). Calcd for $C_{14}H_{19}NO_7$ (313.3): C, 53.67; H, 6.11; N, 4.47; found: C, 53.78; H, 6.22; N, 4.59.

*N-(2-Deoxy-α-L-*arabino*-hexopyranosyl)-succinamic acid allyl ester (21)*

Compound **20** (313 mg, 1.0 mmol) was reacted and worked up as described in the protocol for the preparation of **10**. Purification by flash chromatography (chloroform:methanol, 10:1) gave **21** as colourless material (270 mg, 94 %); mp 83 °C; $[\alpha]_D^{20}$ = −98.0 ° (c = 1.0, CH_3OH); ^1H NMR (CD_3OD): δ = 5.40 (m, H-1), 1.87 (ddd, H-2), 1.70 (ddd, H-2'), 3.70 (ddd, H-3), 3.85 (dd ≈ t, H-4), 3.39 (dq, H-5), 1.10 (d, 3H, H-6), 2.42 and 2.50 (each m, each 2H, CH_2), 4.47 (d, allyl-Hα), 5.82 (m, allyl-Hβ), 5.11 and 5.22 (each dd, each 1H, allyl-Hτ, τ'); $J_{1,2}$ = 0.8, $J_{1,2'}$ = 5.2, $J_{2,2'}$ = 12.8, $J_{2,3}$ = 5.2, $J_{2',3}$ = 12.0, $J_{3,4}$ = 8.8, $J_{4,5}$ = 8.8, $J_{5,6}$ = 6.0, $J_{\beta,\tau\text{-}trans}$ =17.2, $J_{\beta,\tau\text{-}cis}$ = 10.6, $J_{\tau,\tau'\text{-}gem}$ = 5.6 Hz.

*N-(3,4-Di-*O*-acetyl-2-deoxy-α-L-*arabino*-hexopyranosyl)-succinamic acid allyl ester (22)*

Compound **21** (1.35 g, 5.0 mmol) was acetylated and worked up as described for **11**. Flash chromatography (toluene:acetone, 3:1) gave **22** as a syrup (1.67 g, 90 %); $[\alpha]_D^{20}$ = 82.0 ° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 6.82 (d, NH), 5.70 (ddd, H-1), 2.00–2.20 (m, 2H, H-2,-2'), 5.11 (ddd, H-3), 4.74 (dd ≈ t, H-4), 3.78 (dq, H-5), 1.22 (d, 3H, H-6), 1.98, 2.15 (2s, 6H, 2 OAc), 2.54 and 2.73 (each m, each 2H, CH_2), 4.60 (d, 2H, allyl-Hα), 5.91 (m, allyl-Hβ), 5.23 and 5.32 (each dd, each 1H, allyl-H-τ,τ'); $J_{1,NH}$ = 8.0, $J_{1,2}$ = 2.0, $J_{1,2'}$ = 4.0, $J_{2,2'}$ = 13.8, $J_{2,3}$ = 5.6, $J_{2',3}$ = 10.4, $J_{3,4}$ = 8.0, $J_{4,5}$ = 8.0, $J_{5,6}$ = 6.2, $J_{\beta,\tau\text{-}trans}$ = 17.2, $J_{\beta,\tau\text{-}cis}$ = 10.4, $J_{\tau,\tau'\text{-}gem}$ = 5.8 Hz. ^{13}C NMR ($CDCl_3$): δ = 73.95, 73.11, 68.91, 67.37 (C-1, C-3, C-4, C-5), 29.24 (C-2), 17.45 (C-6), 33.56 (CH_2-amide), 30.86 (CH_2-ester), 131.98 (CH_β-allyl), 118.41 (CH_c-allyl), 65.49 (CH_α-allyl), 169.95, 170.54, 171.60, 172.75 (C=O), 20.99, 20.83 (CH_3-acetyl). Calcd for $C_{17}H_{25}NO_8$ (371.4): C, 54.98; H, 6.79; N, 3.77; found: C, 54.85; H, 6.78; N, 3.72.

*N-(3,4-Di-*O*-acetyl-2,6-dideoxy-2-iodo-α-L-talopyranosyl)-succinimide (24)*

3,4-Di-*O*-acetyl-L-fucal (**23**, 2.14 g, 10.0 mmol) was treated with NIS and worked up as given for **4**. Flash chromatography of the raw material gave an amorphous solid (3.3 g, 75 %); mp 85 °C; $[\alpha]_D^{20}$ = +6.9 ° (c = 1.0, acetone); ^1H NMR ($CDCl_3$): δ = 5.76 (d, H-1), 5.52 (dd, H-2), 5.72 (dd, H-3), 5.29 (dd, H-4), 4.42 (dq, H-5), 1.51 (d, 3H, CH_3), 2.72 (s, 4H, CH_2), 2.00, 2.18 (2s, 6H, 2 OAc); $J_{1,2}$ = 10.8, $J_{2,3}$ = 3.2, $J_{3,4}$ = 3.2, $J_{4,5}$ = 6.4, $J_{5,6}$ = 7.2 Hz. ^{13}C NMR (acetone-d_6): δ = 74.29 (C-1), 23.91 (C-2), 71.65, 68.03 (C-3, C-4), 72.11 (C-5), 13.86 (C-6), 28.55 (2 C-imide), 177.17 (s, 2 C=O-imide), 169.80, 169.55 (2 C=O-acetyl), 20.88, 20.58 (2 CH_3-acetyl). Calcd for $C_{14}H_{18}INO_7$ (439.2): C, 38.29, H, 4.13; N, 3.19; I, 28.89; found: C, 38.30; H, 4.18; N, 3.22; I, 28.99.

*N-(3,4-Di-*O*-acetyl-2-deoxy-α-L-*lyxo*-hexopyranosyl)-succinimide (25)*

Compound **24** (2.2 g, 5.0 mmol) were reduced with *n*-Bu_3SnH and worked up as given for **7**. Purification by

flash chromatography (toluene:acetone, 4:1) gave a colourless solid (1.41, 90 %); mp 172 °C; $[\alpha]_D^{20}$ = +11.0 ° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 5.89 (dd, H-1), 2.26 (ddd, H-2), 2.26 (ddd, H-2'), 5.85 (ddd, H-3), 5.23 (dd, H-4), 4.10 (dq, H-5), 1.18 (d, 3H, H-6), 2.73 (s, 4H, CH_2), 1.98–2.05 (2s, 6H, 2 OAc); $J_{1,2}$ = 6.1, $J_{1,2'}$ = 4.0, $J_{2,3}$ = 6.8, $J_{2',3}$ = 6.2, $J_{3,4}$ = 3.6, $J_{4,5}$ = 2.1, $J_{5,6}$ = 6.6 Hz. ^{13}C NMR ($CDCl_3$): δ = 76.67, 70.02, 68.74, 67.60 (C-1, C-3, C-4, C-5), 27.43 (C-2), 16.49 (C-6), 28.13 (2 C-imide), 177.04 (s, 2 C=O-imide), 170.50, 169.90 (2 C=O-acetyl), 20.92, 20.70 (2 CH_3-acetyl). Calcd for $C_{14}H_{19}NO_7$ (313.3): C, 53.67; H, 6.11; N, 4.47; found: C, 53.70; H, 6.18; N, 4.60.

*N-(2-Deoxy-α-L-*lyxo*-hexopyranosyl)-succinamic acid allyl ester (26)*

Ring opening of compound **25** (313 mg, 1.0 mmol) and work up was as for **10**. Purification by flash chromatography gave a syrup (210 mg, 77 %); $[\alpha]_D^{20}$ = –46.0 ° (c = 1.0, CH_3OH); ^1H NMR (CD_3OD): δ = 5.42 (m, H-1), 1.89 (ddd, H-2), 1.74 (ddd, H-2'), 4.00 (ddd, H-3), 3.88 (dd, H-4), 3.42 (dq, H-5), 1.15 (d, 3H, CH_3), 2.53 and 2.60 (each m, each 2H, CH_2), 4.59 (d, 2H, allyl-Hα), 5.95 (m, allyl-Hβ), 5.25 and 5.30 (each dd, each 1H, allyl-Hτ,τ'); $J_{1,2}$ = 0.2, $J_{1,2'}$ = 5.0, $J_{2,2'}$ = 13.0, $J_{2,3}$ = 5.0, $J_{2',3}$ = 12.0, $J_{3,4}$ = 3.0, $J_{4,5}$ = 0.9, $J_{5,6}$ = 6.2, $J_{\beta,\tau\text{-}trans}$ = 17.0, $J_{\beta,\tau\text{-}cis}$ = 10.5, $J_{\tau,\tau\text{-}gem}$ = 5.8 Hz.

*N-(3,4-Di-*O*-acetyl-2-deoxy-α-L-*lyxo*-hexopyranosyl)-succinamic acid allyl ester (27)*

Compound **26** (1.35 g, 5.0 mmol) was acetylated and worked up as for **11**. Flash chromatography gave a syrup (928 mg, 50 %). $[\alpha]_D^{20}$ = –62.0 ° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 6.80 (d, NH), 5.68 (ddd, H-1), 2.00–2.20 (m, 2H, H-2, -2'), 5.28 (ddd, H-3), 5.06 (dd, H-4), 3.85 (dq, H-5), 1.24 (d, 3H, H-6), 1.95–2.10 (2s, 6H, 2 OAc), 2.50 and 2.70 (each m, each 2H, CH_2), 4.60 (d, 2H, allyl-Hα), 5.90 (m, allyl-Hβ), 5.23 and 5.31 (each dd, each 1H, allyl-Hτ,τ'); $J_{1,NH}$ = 8.0, $J_{1,2}$ = 4.2, $J_{1,2'}$ = 1.8, $J_{2,2'}$ = 13.6, $J_{2,3}$ = 9.8, $J_{2',3}$ = 5.2, $J_{3,4}$ = 2.8, $J_{4,5}$ = 0.8, $J_{5,6}$ = 6.2, $J_{\beta,\tau\text{-}trans}$ = 17.2, $J_{\beta,\tau\text{-}cis}$ = 10.4, $J_{\tau,\tau\text{-}gem}$ = 5.6 Hz. Calcd for $C_{17}H_{25}NO_8$ (371.4): C, 54.98; H, 6.79; N, 3.77; found: C, 54.85; H, 6.78; N, 3.72.

*N-[3,6-Di-*O*-acetyl-2-deoxy-2-iodo-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-mannopyranosyl]-succinimide (29)*

Treatment of 3,6,2',3',4',6'-hexa-*O*-acetyl-lactal (5.8 g, 10.0 mmol) with NIS and work up followed the protocol for the preparation of **4**. Flash chromatographic purification (toluene:acetone, 1:1) gave a colourless solid (3.53 g, 45 %); mp 175 °C; $[\alpha]_D^{20}$ = +2.0 ° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$); A-ring: δ = 5.81 (d, H-1), 5.63 (dd, H-2), 5.69 (dd, H-3), 3.75 (dd, H-4), 4.47 (dd, H-5), 4.13 (dd, H-6), 4.24 (dd, H-6'); B-ring: 4.68 (d, H-1), 5.23 (dd, H-2), 5.03 (dd, H-3), 5.39 (dd, H-4), 4.02 (ddd, H-5), 4.13 (m, 2H, H-6, -6'), 2.74 (s, 4H, CH_2), 2.00–2.15 (6s, 18H, 6 × OAc); A-ring: $J_{1,2}$ = 10.7; $J_{2,3}$ = 2.6, $J_{3,4}$ = 1.4, $J_{4,5}$ = 6.6, $J_{5,6}$ = 2.8, $J_{5,6'}$ = 6.8, $J_{6,6'}$ = 11.6, B-ring: $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.2, $J_{4,5}$ = 0.8, $J_{6,6'}$ = 11.6 Hz. ^{13}C NMR ($CDCl_3$): δ = 101.1 (C-1B), 77.54 (C-1A), 18.56 (C-2A), 77.23, 74.02, 73.24, 71.21, 70.91, 68.73, 67.07 (C-3A, C-4A, C-5A, C-2B, C-3B, C-4B, C-5B), 62.99, 60.99 (C-6A, C-6B), 27.94 (2 CH_2-imide), 176.16 (s, 2 C=O-imide), 169.26–170.51 (C=O-acetyl), 20.90–20.56 (CH_3-acetyl). Calcd for $C_{28}H_{36}INO_{17}$ (785.5): C, 42.82; H, 4.62; N, 1.78; I, 16.16; found: C, 42.88; H, 4.56; N, 1.88; I, 16.44.

*N-[3,6-Di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-*arabino*-hexopyranosyl]-succinimide (30)*

Compound **29** (3.93 g, 5.0 mmol) was treated with *n*-Bu_3SnH and worked up as described for **7**. Flash chromatography (toluene:acetone, 1:1) gave pure solid material (2.48, 75 %); mp 89 °C, $[\alpha]_D^{20}$ = +4.0 ° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): A-ring: δ = 5.80 (dd, H-1), 3.03 (ddd, H-2), 1.88 (ddd, H-2'), 5.56 (ddd, H-3), 3.65 (dd, H-4), 4.45 (ddd, H-5), 4.07 (dd, H-6), 4.27 (dd, H-6'); B-ring: 4.70 (d, H-1), 5.21 (dd, H-2), 5.02 (dd, H-3), 5.39 (dd, H-4), 3.97 (ddd, H-5), 4.13 (m, 2H, H-6, H-6'), 2.78 (s, 4H, CH_2), 2.25–1.90 (6s, 18H, 6 × OAc); A-ring: $J_{1,2}$ = 10.8, $J_{1,2'}$ = 5.2, $J_{2,2'}$ = 14.0, $J_{2,3}$ = 3.2, $J_{2',3}$ = 1.2, $J_{3,4}$ = 1.0, $J_{4,5}$ = 8.8, $J_{5,6}$ = 2.4, $J_{5,6'}$ = 5.2, $J_{6,6'}$ = 12.0; B-ring: $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.4, $J_{3,4}$ = 2.4, $J_{4,5}$ = 0.6, $J_{6,6'}$ = 11.6 Hz. ^{13}C NMR ($CDCl_3$): δ = 102.01 (C-1B), 22.61 (C-2A), 66.97–78.11 (C-3A, C-4A, C-5A, C-1B, C-2B, C-3B, C-4B, C-5B), 62.85, 61.02 (C-6A, C-6B), 29.30 (CH_2-imide), 169.4–170.66 (C-O-acetyl), 176.55 (C-O-imide). Calcd for $C_{28}H_{37}NO_{17}$ (659.6): C, 50.99; H, 5.65; N, 2.12; found: C, 51.02; H, 5.79; N, 2.07.

*N-[2-Deoxy-4-*O*-(β-D-galactopyranosyl)-α-D-*arabino*-hexopyranosyl]-succinamic acid allyl ester (31)*

Compound **30** (660 mg, 1.0 mmol) was ring-opened and the reaction mixture worked up as described for **10**. Purification by flash chromatography ($CHCl_3$:MeOH, 4:1) gave an amorphous solid (448 mg, 96 %); mp 113 °C, $[\alpha]_D^{20}$ = +72.0 ° (c = 1.0, CH_3OH); ^1H NMR (D_2O); A-ring: δ = 5.63 (m, H-1), 1.96 (ddd, H-2), 2.17 (ddd, H-2'), 4.11 (ddd, H-3), 3.64 (dd ≈ t, H-4), 3.68 (, 2H, H-5, -6), 3.92 (dd, H-6'); B-ring: 4.51 (d, H-1), 3.62 (dd, H-2), 3.72 (dd, H-3), 3.98 (dd, H-4), 3.80 (m, H-5), 3.80 (m, 2H, H-6, H-6'), 4.62 (d, 2H, allyl-Hα), 6.00 (m, allyl-Hβ), 5.33 and 5.39 (each dd, each 1H, allyl-H-τ, τ'), 2.68 and 2.76 (each m, each 2H, CH_2); A-ring: $J_{1,2}$ = 5.2, $J_{1,2'}$ = 1.2, $J_{2,2'}$ = 13.6, $J_{2,3}$ = 12.0, $J_{2',3}$ = 5.0, $J_{3,4}$ = 8.0, $J_{4,5}$ = 8.0, $J_{5,6'}$ = 3.4, $J_{6,6'}$ = 12.0; B-ring: $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0, $J_{3,4}$ = 3.2, $J_{4,5}$ = 0.6, $J_{6,6'}$ = 12.0, $J_{\beta,\tau\text{-}trans}$ = 17.2, $J_{\beta,\tau\text{-}cis}$ = 8.0, $J_{\tau,\tau\text{-}gem}$ = 5.2 Hz. Calcd for $C_{19}H_{31}NO_{12}$ (456.5): C, 49.03; H, 6.71; N, 3.01; found: C, 49.59; H, 6.42; N, 2.99.

*N-[3,6-Di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-*arabino*-hexopyranosyl]-succinamic acid allyl ester (32)*

Compound **31** (900 mg, 2.0 mmol) was acetylated and worked up as for **11**. Purification by flash chromatography

(toluene:acetone, 1:1) gave a solid foam (1.43 g, 92 %); $[\alpha]_D^{20}$ = +37 ° (c = 1.0, $CHCl_3$), ^1H NMR ($CDCl_3$); A-ring: δ = 5.68 (m, H-1), 1.90–2.10 (m, H-2, -2'), 5.22 (m, H-3), 3.68 (dd ≈ t, H-4), 3.86 (m, H-5), 4.21 (dd, H-6), 4.31 (dd, H-6'); B-ring: 4.65 (d, H-1), 5.14 (dd, H-2), 4.99 (dd, H-3), 5.38 (dd, H-4), 3.19 (ddd, H-5), 4.15 (m, 2H, H-6, H-6'), remaining signals: 6.85 (d, NH) 2.54 and 2.70 (each m, each 2H, CH_2), 2.25–1.90 (6s, 18H, 6 OAc), 4.59 (m, 2H, allyl-Hα), 5.90 (m, allyl-Hβ), 5.24 and 5.32 (each dd, each 2H, allyl-Hτ,τ'); A-ring: $J_{1,NH}$ = 7.6, $J_{1,2}$ = 4.8, $J_{1,2'}$ = 3.0, $J_{2,2'}$ = 13.6, $J_{3,4}$ = 6.8, $J_{4,5}$ = 7.2, $J_{5,6}$ = 5.8, $J_{6,6'}$ = 12.0; B-ring: $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0, $J_{3,4}$ = 3.6, $J_{4,5}$ = 0.4, $J_{5,6}$ = 6.0, $J_{5,6'}$ = 7,2, $J_{6,6'}$ = 11.6; $J_{\beta,\tau\text{-}trans}$ = 17.2, $J_{\beta,\tau\text{-}cis}$ = 10.4, $J_{\tau,\tau'\text{-}gem}$ = 5.6 Hz. Calcd for $C_{31}H_{43}NO_{18}$ (717.7): C, 51.88; H, 6.04; N, 1.95; found: C, 51.93; H, 6.00; N, 1.93.

*N-(3,4,6-Tri-O-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-succinamyl-L-leucine-allyl ester (33)*

Glycoside **12** (200 mg, 0.38 mmol) and L-leucine allyl ester hydrotosylate (127 mg, 0.38 mmol) were dissolved in anhydrous dichloromethane (5 mL), treated with ethyl 2-ethoxy-1,2-dihydroquinoline-1-carboxylate (EEDQ, 93 mg, 0.38 mmol) and triethylamine (38 µL). After 12 h at room temperature the solvent was evaporated and the residue was purified by chromatography with hexane:ethyl ether (1:1) in order to remove the quinoline derivatives. Final elution with toluene:acetone (5:1) gave **33** as a syrup (2.3 mg, 80 %); $[\alpha]_D^{20}$ = +38.0 ° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 5.92 (m, H-1), 1.78 (ddd, H-2), 2.05 (ddd, H-2'), 4.00 (dd, H-3), 3.70 (dd, H-4), 3.89 (ddd, H-5), 3.63 (dd, H-6), 3.75 (dd, H-6'), 7.10 (d, NH-spacer), 4.70 (mc, 1H, CHα-Leu), 1.55 (mc, 3H, CHβ-Leu, CHτ-Leu), 0.90 (mc, 6H, 2 CH_3-Leu), 7.90 (d, 1H, NH-Leu), 2.44 (mc, 4H, 2 CH_2-spacer), 4.30–4.55 (m, 8H, 3 CH_2-Ph, allyl-Hα), 5.58 (m, 1H, allyl-Hβ), 4.84 (d, 1H, allyl-Hτ,*cis*), 5.00 (d, allyl-Hτ,*trans*), 7.00 (mc, 15H, aryl-H); $J_{1,NH}$ = 8.5, $J_{1,2}$ = 5.0, $J_{1,2'}$ = 0.4, $J_{2,2'}$ = 14.0, $J_{2,3}$ = 10.0, $J_{2',3}$ = 3.0, $J_{3,4}$ = 9.6, $J_{4,5}$ = 10.0, $J_{5,6'}$ = 4.0, $J_{6,6'}$ = 11.4, $J_{NH,CH\alpha\text{-}Leu}$ = 8.4, $J_{H\alpha,gem}$ = 5.2, $J_{H\beta\text{-}\tau\text{-}cis}$ = 6.2, $J_{H\beta,\tau\text{-}trans}$ = 17.0 Hz. Calcd for $C_{40}H_{50}N_2O_8$ (686.9): C, 69.95; H, 7.34; N, 4.08; found: C, 70.02; H, 7.26; N, 3.69.

*N-(2-Deoxy-α-D-*arabino*-hexopyranosyl)-succinamyl-L-leucine-propyl ester (34)*

Compound **33** (60 mg, 0.09 mmol) was dissolved in methanol (20 mL), Pd/C (10 %) added and hydrogenated for 12 h under normal pressure. After evaporation the raw material was purified chromatographically with methanol to give an amorphous solid (36 mg, 96 %); $[\alpha]_D^{20}$ = +12.0 ° (c = 1.0, $CHCl_3$); ^1H NMR (MeOD): δ = 5.50 (dd, H-1), 1.90 (ddd, H-2), 2.05 (ddd, H-2'), 3.80 (dd, H-3), 3.20–3.60 (mc, 4H, H-4, H-5, H-6, H-6'), 4.45 (mc, 1H, CH_α-Leu), 1.80 (mc, 5H, CH_β-Leu, CH_τ-Leu, $CH_{2\text{-}\beta}$-propyl), 0.92 (mc, 9H, 2 CH_3-Leu, CH_3-propyl), 2.50 (mc, 4H, 2 CH_2-spacer), 4.00 (t, 2H, $CH_{2\text{-}\alpha}$-propyl); $J_{1,2}$ = 5.0, $J_{1,2'}$ = 0.0, $J_{2,2'}$ = 14.0, $J_{2,3}$ = 4.8 Hz.

N-(3,4,6-Tri-O-benzyl-2-deoxy-α-D-arabino-hexopyranosyl)-succinamyl-L-seryl-L-phenylalanyl-L-leucine-propyl ester (35)

Glycoside **12** (200 mg, 0.37 mmol) and peptide H-Ser-Phe-Leu-OPropyl (154 mg, 0.38 mmol) were dissolved in anhydrous dichloromethane (10 mL) and EEDQ (93 mg, 0.38 mmol) added. Triethylamine (35 µL) was added and after 6 h at room temperature the product was purified by chromatography. Elution with hexane:ethyl ether (1:1) removed quinoline derivatives and elution with chloroform:methanol (20:1) gave compound **35** as a syrup (255 mg, 73 %); $[\alpha]_D^{20}$ = +1.8 ° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 5.63 (t, H-1), 1.82 (ddd, H-2), 2.13 (ddd, H-2'), 3.97 (m, H-3), 3.52 (t, H-4), 3.67 (m, 3H, H-5, H-6, H-6'), 4.60 (mc, CH_α-Ser), 3.23 (dd, CH_β-Ser), 3.06 (dd, CH_β,-Ser), 4.25 (mc, CH_α-Phe), 3.50 (mc, 2H, CH_β-Phe), 4.48 (mc, CH_α-Leu), 1.55 (mc, 3H, CH_β-Leu, CH_τ-Leu), 0.90 (mc, 6H, 2 CH_3-Leu), 2.55, 2.77 (mc, 4H, 2 CH_2-spacer), 4.03 (t, 2H, CH_2-α-propyl), 1.55 (m, 2H, CH_2-β-propyl), 0.94 (t, 3H, CH_3-propyl), 4.40–4.80 (m, 6H, CH_2-Ph), 7.30 (mc, 20H, aryl-H); $J_{1,2}$ = 4.5, $J_{1,2'}$ = 3.5, $J_{2,2'}$ = 13.4, $J_{2,3}$ = 3.5, $J_{3,4}$ = 10.0, $J_{4,5}$ = 9.6, $J_{CH\alpha,\beta\text{-}Ser}$ = 4.0, $J_{CH\alpha,\beta'\text{-}Ser}$ = 10.0, $J_{CH\beta,\beta'\text{-}Ser}$ = 13.8 Hz.

*N-(2-Deoxy-α-D-*arabino*-hexopyranosyl)-succinamyl-L-seryl-L-phenylalanyl-L-leucine-propyl ester (36)*

Compound **35** (40 mg, 0.04 mmol) was hydrogenated as described for **34**. By chromatography on silica gel (methanol) **36** was obtained pure (26 mg, 95 %); $[\alpha]_D^{20}$ = –4.0 ° (c = 0.5, CH_3OH); ^1H NMR (MeOD): δ = 5.50 (m, H-1), 2.02, 1.80 (m, 2H, H-2, H-2'), 3.80 (m, H-3), 3.40–3.60 (m, 4H, H-4, H-5, H-6, H-6'), 4.23 (mc, CH_α-Ser), 4.42 (mc, CH_α-Phe), 3.00, 3.20 (mc, 2H, CH_β-Phe), 4.42 (mc, CH_α-Leu), 1.80–0.95 (m, 9H, CH_3-Leu, CH_β-Leu, CH_τ-Leu), 2.50 (mc, 4H, CH_2-CH_2-spacer), 4.05 (t, 2H, $CH_{2\text{-}\alpha}$-propyl), 1.68 (m, 2H, $CH_{2\text{-}\beta}$-propyl), 0.98 (t, 3H, CH_3-propyl), 7.30 (mc, 5H, aryl-H).

*N-(3,4,6-Tri-O-acetyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-succinamyl-L-seryl-L-phenylalanyl-L-leucine-propyl ester (37)*

Compound **11** (163 mg, 0.38 mmol) was dissolved in anhydrous THF (5 mL) under argon cover and treated with tetrakis–palladium triphenylphosphane complex (46.2 mg, 0.04 mmol). Following addition of morpholine (0.5 mL, 5.7 mmol) the mixture was stirred for 30 min. THF and morpholine were evaporated (in high *vacuo*), the residue taken up in chloroform (10 mL), washed twice with hydrochloric acid (0.5 N), dried ($MgSO_4$), filtered and evaporated to give the non-purified acid intermediate (118 mg, 80 %). This was dissolved with peptide H-Ser-Phe-Leu-OPropyl (122 mg, 0.3 mmol) and EEDQ (73 mg, 0.3 mmol) in anhydrous CH_2Cl_2 (5 mL). Following addition of triethylamine (35 µL) the mixture was left at room temperature for 48 h. After evaporation, chromatography with hexane:ethyl ether (1:1) eluted quinoline residues and elution with $CHCl_3$:CH_3OH (10:1) gave **37** (126 mg, 55

%); $[\alpha]_D^{20}$ = +13.0 ° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 5.75 (m, H-1), 2.20 (m, 2H, H-2, H-2'), 5.21 (m, H-3), 5.01(t, H-4), 3.92 (m, H-5), 4.05 (dd, H-6), 4.28 (dd, H-6'), 7.68 (d, NH-spacer), 4.75 (mc, 1H, CH_α-Ser), 3.20 (dd, CH_β-Ser), 3.08 (dd, CH_β-Ser), 7.41 (d, NH-Ser), 3.20 (m, OH-Ser), 4.50 (mc, CH_α-Phe), 3.90, 3.60 (2mc, 2H, CH_β-Phe), 6.90 (d, NH-Phe), 4.50 (mc, CH_α-Leu), 1.60 (mc, 3H, CH_β-Leu, CH_γ-Leu), 0.90 (mc, 6H, 2 CH_3-Leu), 6.90 (d, NH-Leu), 2.55 (mc, 4H, 2 CH_2-spacer), 4.05 (t, 2H, $CH_{2\text{-}\alpha}$-propyl), 1.65 (m, 2H, $CH_{2\text{-}\beta}$-propyl), 0.94 (t, 3H, CH_3-propyl), 2.00, 2.01, 2.02 (3s, 9H, 3 OAc), 7.30 (mc, 5H, aryl-H); $J_{1,NH}$ = 8.1, $J_{1,2}$ = 2.0, $J_{1,2'}$ = 0.0, $J_{2,3}$ = 10.0, $J_{2',3}$ = 5.0, $J_{3,4}$ = 10.0, $J_{4,5}$ = 10.0, $J_{5,6'}$ = 4.6, $J_{6,6'}$ = 12.6, $J_{NH,CH\alpha\text{-Leu}}$ = 8.2, $J_{NH,CH\alpha\text{-Ser}}$ = 8.6, $J_{NH,CH\alpha\text{-Phe}}$ = 8.4, $J_{CH\alpha,\beta\text{-Ser}}$ = 5.6, $J_{CH\alpha,\beta'\text{-Ser}}$ = 8.0, $J_{CH\beta,\beta'\text{-Ser}}$ = 12.8 Hz.

*N-(3,4,6-Tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-succinamyl-L-seryl-[(3S,4S)-4-amino-5-cyclohexyl-3-hydroxy-pentanoyl]-L-isoleucine methyl ester (38)*

Glycoside **12** (200 mg, 0.38 mmol) and peptide H-Ser-ACHPA-Ile-OMe (163 mg, 0.38 mmol) in anhydrous CH_2Cl_2 (5 mL) were treated with EEDQ (93 mg, 0.38 mmol) and triethylamine (35 μL) for 6 h at room temperature. Work up and purification as described for **35** gave product **38** (226 mg, 60 %); $[\alpha]_D^{20}$ = +4.0 ° (c = 0.5, CH_3OH); ^1H NMR (CD_3OD): δ = 5.66 (t, H-1), 2.18 (m, H-2), 2.00 (ddd, H-2'), 4.02 (m, H-3), 3.53 (t, H-4), 3.70 (mc, 3H, H-5, H-6, H-6'), 4.38 (mc, CH_α-Ser), 3.87 (dd, CH_β-Ser), 3.85 (dd, CH_β-Ser), 3.68 (m, NH-CH_{ACHPA}), 3.98 (m, $CH(OH)_{ACHPA}$), 2.35 (m, 2H, CH_2-$C{=}O_{ACHPA}$), 1.95–0.80 (m, 19H, CH_3-, CH_2-ACHPA, CH_3-, CH_2-, CH_β-Ile), 4.38 (m, CH_α-Ile), 3.69 (s, 3H, OCH_2), 2.60 (m, 4H, CH_2-CH_2-spacer), 4.40–4.80 (m, 6H, CH_2-Ph), 7.10–7.30 (m, 15H, aryl-H); $J_{1,2}$ = 5.0, $J_{1,2'}$ = 0.8, $J_{2,2'}$ = 13.4, $J_{2,3}$ = 10.0, $J_{2',3}$ = 5.0, $J_{3,4}$ = 8.0, $J_{4,5}$ = 8.0, $J_{CH\alpha,\beta\text{-Ser}}$ = 3.0, $J_{CH\alpha,\beta'\text{-Ser}}$ = 7.0, $J_{CH\beta,\beta'\text{-Ser}}$ = 12.6 Hz.

*N-(2-Deoxy-α-D-*arabino*-hexopyranosyl)-succinamyl-L-seryl-[(3S,4S)-4-amino-5-cyclohexyl-3-hydroxy-pentanoyl]-isoleucine methyl ester (39)*

Compound **38** (100 mg, 0.11 mmol) was hydrogenolised as described for **36** to give the unblocked derivative **39** (64 mg, 86 %); $[\alpha]_D^{20}$ = +8.0 ° (c = 0.5, CH_3OH); ^1H NMR (CD_3OD): δ = 5.55 (dd, H-1), 2.06, 1.90 (m, 2H, H-2, H-2'), 3.85 (m, H-3), 3.80–4.00 (m, 3H, H-4, H-6, H-6'), 3.55 (m, H-5), 4.20–4.40 (m, 2H, CH_α-Ser, CH_α-Ile), 3.90 (m, 2H, CH_β-Ser), 3.60 (m, NH-CH_{ACHPA}), 3.95 (m, $CH(OH)_{ACHPA}$), 2.70 (m, 2H, CH_2-$C{=}O_{ACHPA}$), 0.80–1.95 (m, 19H, CH_3-CH_2-ACHPA- CH_3-, CH_2-, CH_β-Ile), 3.60 (s, 3H), 2.50 (m, 4H, CH_2-CH_2-spacer); $J_{1,2}$ = 5.0, $J_{1,2'}$ = 0.8, $J_{2,2'}$ = 13.4, $J_{2,3}$ = 10.0 Hz.

*N-(3,4,6-Tri-*O*-benzyl-2-deoxy-α-*arabino*-hexopyranosyl)-succinamyl-L-seryl-L-leucyl-[(3S,4S)-4-amino-5-cyclohexyl-3-hydroxy-pentanoyl]-L-isoleucine methyl ester (40)*

Glycoside **12** (200 mg, 0.38 mmol) and peptide H-Ser-Leu-ACHPA-Ile-OMe (206 mg, 0.38 mmol) in anhydrous CH_2Cl_2 (5 mL) were treated with EEDQ (93 mg, 0.38 mmol) and triethylamine (35 μL) for 6 h at room temperature. Work up was as for **35**; elution with hexane:ethyl ether (1:1) removed quinoline derivatives and final elution with chloroform:methanol (25:1) gave **40** (301 mg, 75 %); $[\alpha]_D^{20}$ = +25.0 ° (c = 1.75, CH_3OH); ^1H NMR (CD_3OD): δ = 5.58 (dd, H-1), 2.16, 1.82 (m, 2H, H-2, H-2'), 3.95 (ddd ≈ dt, H-3), 3.55 (m, H-4), 3.69 (m, H-5), 3.62, 3.72 (each m, 2H, H-6, H-6'), 4.30 (mc, CH_α-Ser), 3.82 (dd, CH_β-Ser), 3.90 (dd, $CH_{\beta'}$-Ser), 4.37 (m, CH_α-Leu), 4.40 (m, CH_α-Ile), 3.66 (m, NH-CH_{ACHPA}), 3.96 (m, $CH(OH)_{ACHPA}$), 2.45 (m, 2H, CH_2-$C{=}O_{ACHPA}$), 0.80–1.95 (m, 31H, CH_3-CH_2-ACHPA, CH_3-, CH_2-, CH_β-Ile, CH_3-, CH_β-Leu), 3.69 (s, 3H, OCH_3), 2.60 (m, 4H, CH_2-CH_2-spacer), 4.45–4.80 (m, 6H, 3 CH_2-Ph), 7.10–7.30 (m, 15H, aryl-H); $J_{1,2}$ = 5.0, $J_{1,2'}$ = 2.6 $J_{2,2'}$ = 13.1, $J_{2,3}$ = 10.0, $J_{2',3}$ = 4.8, $J_{CH\alpha,\beta\text{-Ser}}$ = 4.5, $J_{CH\alpha,\beta'\text{-Ser}}$ = 4.5, $J_{CH\beta,\beta'\text{-Ser}}$ = 12.0 Hz.

*N-(2-Deoxy-α-D-*arabino*-hexopyranosyl)-succinamyl-L-seryl-L-leucyl-[(3S,4S)-4-amino-5-cyclohexyl-3-hydroxy-pentanoyl]-L-isoleucine methyl ester (41)*

Compound **40** (180 mg, 0.17 mmol) was hydrogenolised as described for **36** to give the unprotected derivative **41** (120 mg, 90 %); $[\alpha]_D^{20}$ = −17.0 ° (c = 1.0, CH_3OH); ^1H NMR (CD_3OD): δ = 5.55 (dd, H-1),1.95–2.08 (m, H-2, H-2'), 3.85 (m, H-3), 3.80–4.00 (m, 3H, H-4, H-6, H-6'), 3.50 (m, H-5), 4.20–4.40 (m, 3H, CH_α-Ser, CH_α-Ile, CH_α-Leu), 3.90 (m, 2H, CH_β-Ser), 3.60 (m, NH-CH_{ACHPA}), 3.95 (m, $CH(OH)_{ACHPA}$), 2.70 (m, 2H, $CH_2C{=}O_{ACHPA}$), 0.80–1.95 (m, 31H, CH_3-, CH_2-ACHPA, CH_3-, CH_2-,CH_β-Ile, CH_3-, CH_2-, CH_β-Leu), 3.60 (s, 3H, OMe), 2.50 (m, 4H, CH_2-CH_2-spacer).

*N-(3,4,6-Tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-succinamyl-L-seryl-L-leucyl-L-phenylalanyl-[(3S,4S)-4-amino-5-cyclohexyl-3-hydroxy-pentanoyl]-L-isoleucine methyl ester (42)*

Glycoside **17** (200 mg, 0.38 mmol) and peptide H-Ser-Phe-Leu-ACHPA-Ile-OMe (262 mg, 0.38 mmol) in anhydrous CH_2Cl_2 (5 mL) were treated with EEDQ (93 mg, 0.38 mmol) and triethylamine for 6 h at room temperature. Work up as for **35** was followed by elution of quinoline derivatives using hexane:ethyl ether (1:1). Product **42** was eluted with $CHCl_3$:CH_3OH (30:1) (295 mg, 65 %); $[\alpha]_D^{20}$ = +9.0 ° (c = 0.7, CH_3OH); ^1H NMR (CD_3OD): δ = 5.56 (dd, H-1), 2.15, 1.85 (m, 2H, H-2, H-2'), 3.95 (m, H-3), 3.56 (t, H-4), 3.81 (m, H-5), 3.68, 3.72 (dd, 2H, H-6, H-6'), 4.20 (mc, 1H, CH_α-Ser), 3.70 (m. 2H. CH_β-Ser), 4.41 (m, CH_α-Leu), 4.40 (m, CH_α-Ile), 4.42 (m, CH_α-Phe), 3.20 (m, 2H, CH_2-Phe), 3.68 (m, NH-CH_{ACHPA}), 3.96 (m, $CH(OH)_{ACHPA}$), 2.60 (m, 2H, CH_2-$C{=}O_{ACHPA}$), 0.80–1.95 (m, 31H, CH_3-, CH_2-ACHPA, CH_3-, CH_2-, CH_β-Ile, CH_3-, CH_2-, CH_β-Leu), 3.70 (s, 3H, OCH_3), 2.45 (m, 4H, CH_2-CH_2-spacer), 4.45–4.80 (m, 6H, 3 CH_2-Ph), 7.10–7.30 (m, 15H, aryl-H); $J_{1,2}$ = 5.0, $J_{1,2'}$ = 2.8, $J_{2,2'}$ = 13.6, $J_{2',3}$ = 4.5 Hz.

*N-{3-O-[4-O-(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-3,6-di-O-acetyl-2-deoxy-2-iodo-α-D-mannopyranosyl]-2,6-dideoxy-α-L-*arabino*-hexopyranosyl}-succinamic acid allyl ester (**43**) and N-{4-O-[4-O-(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-3,6-di-O-acetyl-2-deoxy-2-iodo-α-D-mannopyranosyl]-2,6-dideoxy-α-L-*arabino*-hexopyranosyl}-succinamic acid allyl ester*

Hexacetyllactal **28** (1.28 g, 2.2 mmol) and compound **21** (300 mg, 1.1 mmol) dissolved in anhydrous acetonitrile (1.5 mL) were treated with molecular sieves (3 Å) and NIS (0.6 g, 2.7 mmol) under nitrogen at room temperature for 30 h. The mixture was diluted with chloroform (30 mL), washed with aqueous sodium hydrogen sulfite (10 %), sodium carbonate, dried ($MgSO_4$) and evaporated. Chromatography (toluene:acetone, 5:2) gave as first fraction compound **43** as a crystalline solid (382 mg, 40 %); mp 109 °C; $[\alpha]_D^{20}$ = –10.5 ° (c = 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 6.67 (d, NH); A-ring: 5.67 (ddd, H-1), 1.95–2.00 (m, 2H, H-2, H-2'), 3.68 (ddd, H-3), 3.17 (dd, H-4), 3.49 (ddd, H-5), 1.32 (d, 3H, CH_3); B-ring: 5.24 (d, H-1), 4.44 (dd, H-2), 5.00 (dd, H-3), 3.85 (dd, H-4), 4.20 (mc, 3H, H-5, H-6, H-6'); C-ring: 4.60 (d, H-1), 5.15 (dd, H-2), 5.02 (dd, H-3), 5.38 (dd, H-4), 3.95 (ddd, H-5), 4.20 (mc, 2H, H-6, H-6'), 1.90–2.25 (m, 18H, 6 OAc), 2.45–2.70 (2mc, 4H, CH_2-spacer), 4.60 (dd, 2H, CH_α-allyl), 5.90 (m, CH_β-allyl), 4.32 (d, $CH_{\tau,trans}$-allyl), 4.25 (d, $CH_{\tau,cis}$-allyl); A-ring: $J_{1,NH}$ = 7.2, $J_{1,2}$ = 5.2, $J_{1,2'}$ = 1.0, $J_{2,2'}$ = 13.6, $J_{3,4}$ = 7.2, $J_{4,5}$ = 8.8, $J_{5,6}$ = 6.2; B-ring: $J_{1,2}$ = 4.0, $J_{2,3}$ = 4.0, $J_{4,5}$ = 8.8, $J_{5,6}$ = 7.0, $J_{5,6'}$ = 3.2, $J_{6,6'}$ = 11.6; C-ring: $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0, $J_{3,4}$ = 3.6, $J_{4,5}$ = 0.4, $J_{5,6}$ = 6.0, $J_{5,6'}$ = 7.2, $J_{6,6'}$ = 11.6, $J_{CH\alpha,gem\text{-allyl}}$ = 5.2, $J_{CH\beta,\tau\text{-}cis\text{-allyl}}$ = 10.6, $J_{CH\beta,\tau\text{-}trans\text{-allyl}}$ = 17.0 Hz.

As second fraction and side product (97 mg, 10 %) the 1' → 4 interglycosidic linkage isomer of **43** was obtained as a syrup; $[\alpha]_D^{20}$ = +5.0 ° (c = 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 6.64 (d, NH); A-ring: 5.66 (ddd, H-1), 2.02, 1.89 (m, 2H, H-2, H-2'), 3.80 (ddd, H-3), 3.07 (dd, H-4), 3.40 (ddd, H-5), 1.32 (d, 3H, CH_3); B-ring: 5.26 (d, H-1), 4.47 (dd, H-2), 5.00 (dd, H-3), 3.85 (dd, H-4), 4.15 (mc, 3H, H-5, H-6, H-6'); C-ring: 4.60 (d, H-1), 5.16 (dd, H-2), 4.99 (dd, H-3), 5.38 (dd, H-4), 3.19 (ddd, H-5), 4.15 (m, 2H, H-6, H-6'); 1.90–2.25 (6s, 18H, 6 OAc), 2.74 (mc, CH_2-spacer), 2.55 (mc, 2H, CH_2-spacer), 4.60 (m, 2H, CH_α-allyl), 5.91 (m, 1H, CH_β-allyl), 5.32 (d, 1H, $CH_{\tau,trans}$-allyl), 5.26 (d, 1H, $CH_{\tau,trans}$-allyl); $J_{1,NH}$ = 7.6, $J_{1,2}$ = 4.4, $J_{1,2'}$ = 0.8, $J_{2,2'}$ = 13.4, $J_{2,3}$ = 8.0, $J_{2',3}$ = 3.8, $J_{3,4}$ = 9.4, $J_{4,5}$ = 8.4, $J_{5,6}$ = 6.4; B-ring: $J_{1,2}$ = 4.0, $J_{2,3}$ = 4.4, $J_{3,4}$ = 6.0, $J_{4,5}$ = 9.2, $J_{5,6}$ = 6.0, $J_{5,6'}$ = 3.2, $J_{6,6'}$ = 11.6; C-ring: $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0, $J_{3,4}$ = 3.6, $J_{4,5}$ = 0.4, $J_{5,6}$ = 6.8, $J_{5,6'}$ = 3.2, $J_{6,6'}$ = 11.6, $J_{CH\alpha,gem\text{-allyl}}$ = 5.2, $J_{CH\beta,\tau\text{-}cis\text{-allyl}}$ = 10.6, $J_{CH\beta,trans\text{-allyl}}$ = 17.0 Hz. Calcd for $C_{37}H_{52}INO_{21}$ (973.7): C, 45.64; H, 5.38; I, 13.03; N, 1.44; found: C, 46.58; H, 5.47; I, 13.67; N, 1.46.

*N-{3-O-[4-O-(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-3,6-di-O-acetyl-2-deoxy-2-iodo-α-D-mannopyranosyl]-4-O-acetyl-2,6-dideoxy-α-L-*arabino*-hexopyranosyl}-succinamic acid allyl ester (**44**)*

Compound **43** (409 mg, 0.46 mmol) was acetylated and worked up as described for compound **11** to give syrupy **44** (318 mg, 74 %); $[\alpha]_D^{20}$ = –8.2 ° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 6.64 (d, NH); A-ring: 5.68 (ddd, H-1), 2.10, 1.95 (m, 2H, H-2, H-2'), 3.75 (m, H-3), 4.70 (dd, H-4), 3.94 (ddd, H-5), 1.32 (d, 3H, CH_3); B-ring: 5.20 (d, H-1), 4.45 (dd, H-2), 5.00 (dd, H-3), 3.71 (dd, H-4), 4.14 (m, 3H, H-5,H-6, H-6'); C-ring: 4.60 (d, H-1), 5.12 (dd, H-2), 5.00 (dd, H-3), 5.35 (dd, H-4), 3.49 (ddd, H-5), 4.12 (m, 2H, H-6, H-6'); 1.90-2.25 (7s, 21H, 7 OAc), 2.73 (mc, 2H, CH_2-spacer), 2.51 (mc, 2H, CH_2-spacer), 4.60 (m, 2H, CH_α-allyl), 5.91 (m, 1H, CH_β-allyl), 5.32 (d, 1H, $CH_{\tau,trans}$-allyl), 5.25 (d, 1H, $CH_{\tau,cis}$-allyl); $J_{1,NH}$ = 8.0; A-ring: $J_{1,2}$ = 8.0, $J_{1,2'}$ = 8.0, $J_{2,2'}$ = 8.0, $J_{2,3}$ = 10.0, $J_{2',3}$ = 10.0, $J_{3,4}$ = 3.6, $J_{4,5}$ = 0.4, $J_{5,6}$ = 6.0, $J_{5,6'}$ = 7.2, $J_{6,6'}$ = 11.6; B-ring: $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0, $J_{3,4}$ = 3.6, $J_{4,5}$ = 0.4, $J_{5,6}$ = 6.0, $J_{5,6'}$ = 7.2, $J_{6,6'}$ = 11.6; C-ring: $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0, $J_{3,4}$ = 3.6, $J_{4,5}$ = 0.4, $J_{5,6}$ = 6.0, $J_{5,6'}$ = 7.2, $J_{6,6'}$ = 11.6, $J_{CH\alpha,gem\text{-allyl}}$ = 5.2, $J_{CH\alpha,\tau\text{-}cis\text{-allyl}}$ = 6.2, $J_{CH\beta,\tau\text{-}trans\text{-allyl}}$ = 17.0 Hz. Calcd for $C_{39}H_{54}INO_{22}$ (1015.8): C, 46.12; H, 5.36; I, 12.49; N, 1.38; found: C, 46.01; H, 5.00; I, 13.40; N, 1.46.

*N-{3-O-[4-O-(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-3,6-di-O-acetyl-2-deoxy-2-iodo-α-D-mannopyranosyl]-4-O-acetyl-2,6-dideoxy-α-L-*arabino*-hexopyranosyl}-succinamic acid L-valine-benzyl ester (**45**)*

Compound **44** (100 mg, 0.11 mmol) dissolved in anhydrous THF (10 mL) was treated with $Pd[P(C_6H_5)_3]_4$ (11.6 mg, 0.01 mmol) and morpholine (0.2 mL, 3.29 mmol) for 30 min at room temperature. THF was evaporated, the residue taken up in methanol, acidified with Amberlite IR 120 H^+ to pH 4 and quickly filtered. Methanol was evaporated, the intermediate compound checked by TLC ($CHCl_3$:CH_3OH, 3:1, one spot only) and directly further converted. Following solution in CH_2Cl_2 (5 mL) under argon Val-OBn* HCl (46 mg, 0.2 mmol), EEDQ (50 mg, 0.2 mmol) and triethylamine (28 µL, 0.2 mmol) were added and the mixture stirred at room temperature for 12 h. After evaporation and chromatography (toluene:acetone, 2:1) compound **45** (79.2 mg, 62 %) was obtained; $[\alpha]_D^{20}$ = +1 ° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 6.40 (d, NH); A-ring: 5.65 (ddd, H-1), 1.90–2.20 (m, 2H, H-2, H-2'), 3.58 (m, H-3), 5.04 (dd, H-4), 3.65 (ddd, H-5), 1.20 (d, 3H, CH_3); B-ring: 5.65 (d, H-1), 4.44 (dd, H-2), 4.79 (dd, H-3), 3.95 (m, 2H, H-4, H-5), 4.20 (m, 2H, H-6, H-6'); C-ring: 4.60 (d, H-1), 5.12 (dd, H-2), 5.00 (dd, H-3), 5.36 (dd, H-4), 3.19 (ddd, H-5), 4.20 (m, 2H, H-6, H-6'); 1.90-2.25 (7s, 21H, 7 OAc), 2.60 (mc, 2H, CH_2-spacer), 2.50 (mc, 2H, CH_2-spacer), 4.60 (m, 2H, CH_α-allyl),5.91 (m, 1H, CH_β-allyl), 5.32 (d, 1H, $CH_{\tau,trans}$-allyl), 5.25 (d, 1H, $CH_{\tau,cis}$-allyl), 7.40 (d, NH_{Val}), 4.48 (m, CH_α-Val), 0.91, 0.86 (2d, 6H, CH_3-Val), 7.20 (m, 5H, aryl-H); A-ring: $J_{1,NH}$ = 8.4, $J_{1,2}$ = 4.4, $J_{1,2'}$ = 0.4, $J_{2,2'}$ = 13.0, $J_{2,3}$ = 8.0, $J_{2',3}$ = 3.6, $J_{3,4}$ = 9.2, $J_{4,5}$ = 10.0, $J_{5,6}$ = 6.4; B-ring: $J_{1,2}$ = 3.6, $J_{2,3}$ = 4.0, $J_{3,4}$ = 9.6, $J_{4,5}$ = 10.0; C-ring: $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0, $J_{3,4}$ = 3.6, $J_{4,5}$ = 0.4, $J_{5,6}$ = 6.0, $J_{5,6'}$ = 7.2, $J_{6,6'}$ = 11.6; $J_{CH\alpha,gem\text{-allyl}}$ = 5.2, $J_{CH\beta,\tau\text{-}cis\text{-allyl}}$ = 12.4, $J_{CH\beta,\tau\text{-}trans\text{-allyl}}$ = 17.0 Hz. Calcd for $C_{48}H_{65}IN_2O_{23}$ (1165.0): C, 49.49; H, 5.62; I, 10.89; found: C, 48.60; H, 5.90; I, 10.90.

*N-(2-Deoxy-α-D-*arabino*-hexopyranosyl)-succinimide (46)*

To a stirred solution of methanol (10 mL), ethyl acetate (5 mL), acetic acid (5 mL) and **8** (500 mg, 0.97 mmol) in an autoclave Pd/C (10 %, 100 mg) was added. At room temperature the hydrogen pressure was kept above 70 bar for 24 h. The reaction mixture was filtered through Celite, codistilled with toluene (2 × 100 mL) to yield pure **46** (237 mg, quant.) as a white solid; mp 135 °C; $[\alpha]_D^{20}$ = –43 ° (c = 1.02, $CHCl_3$); ^1H NMR (CD_3OD): δ = 5.58 (dd, H-1), 2.43 (ddd, H-2), 1.88 (ddd, H-2'), 4.24 (ddd, H-3), 3.31 (dd, H-4), 3.44 (ddd, H-5), 3.62, 3.63 (m, 2H, H-6, H-6'), 2.65 (s, 4H, CH_2); $J_{1,2}$ = 7.0, $J_{1,2'}$ = 3.0, $J_{2,2'}$ = 14.5, $J_{2,3}$ = 5.5, $J_{2',3}$ = 9.5, $J_{3,4}$ = 8.0, $J_{4,5}$ = 9.0, $J_{5,6}$' = 5.0; ^{13}C NMR (D_2O, CH_3CN): δ = 27.24 (2C, CH_2, imide), 31.09 (CH_2, C-2), 59.71 (CH_2, C-6), 68.93, 69.29 (2C, CH, C-4, C-5), 74.29, 75.31 (2C, CH, C-1, C-3), 180.30 (2C, q, C=O imide). Calcd for $C_{10}H_{15}NO_6$ (245.2): C, 48.98; H, 6.17; N, 5.71; found: C, 48.92; H, 6.21; N, 5.65.

*N-(4,6-*O*-Isopropylidene-2-deoxy-α-D-*arabino*-hexopyranosyl)-succinimide (47)*

Catalytic amounts of *p*-TsOH were added at room temperature to a solution of **46** (0.46 g, 1.88 mmol) in acetone (10 mL) and 2,2-dimethoxypropane (1 mL). After stirring overnight the reaction mixture was concentrated, carefully neutralized with Amberlite IRA 68 and the crude product crystallized from dry ethyl acetate to yield **47** (508 mg, 95 %); mp 163–165 °C; $[\alpha]_D^{20}$ = +60 ° (c = 0.85, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 5.74 (dd, H-1), 2.14 (ddd, H-2), 2.42 (ddd, H-2'), 4.61 (m, H-3), 3.57 (dd, H-4), 3.45 (ddd, H-5), 3.63 (dd, H-6), 3.79 (dd, H-6'), 2.51 (d, OH), 2.73 (s, 4H, imide), 1.41 (s, 3H, *i*-prop), 1.51 (s, 3H, *i*-prop), 2.51 (d, OH); $J_{1,2}$ = 1.0, $J_{1,2'}$ = 7.5, $J_{2,2'}$ = 14.0, $J_{2,3}$ = 6.0, $J_{2',3}$ = 10.0, $J_{3,4}$ = 9.0, $J_{3,OH}$ = < 0.5, $J_{4,5}$ = 10.5, $J_{5,6}$ = 10.0, $J_{5,6}$' = 5.6, $J_{6,6'}$ = 11.0; ^{13}C NMR ($CDCl_3$): δ = 19.11 (CH_3, *i*-prop), 28.15 (2C, CH_2, imide), 29.07 (CH_3, *i*-prop), 33.55 (C-2), 62.06 (C-6), 66.79, 67.52, 75.27, 75.52 (C-3, C-4, C-5, C-1), 99.52 (*i*-prop), 176.36 (2C, imide C=O). Calcd for $C_{13}H_{19}NO_6$ (285.3): C, 54.73; H, 6.71; N, 4.91; found: C, 54.62; H, 6.71; N, 4.78.

*N-[2-Deoxy-3,4,6-tris-(trimethylsilyl)-α-D-*arabino*-hexopyranosyl]-succinimide (48)*

At –80 °C bis(trimethylsilyl)acetamide (95 %, 5.9 mL, 23 mmol) was added slowly to a solution of dry THF, pyridine (30 mL, 42 mmol) and **46** (1.713 g, 7.0 mmol). The solution was slowly allowed to warm to room temperature and stirred overnight. Pyridine and THF were evaporated and the residue was taken up in ether (50 mL). The organic phase was washed with water (3 × 30 mL), $NaHCO_3$ solution (30 mL), and brine (30 mL), dried (Na_2SO_4) and concentrated. The crude oil was purified by flash chromatography (toluene:ethyl acetate, 4:1) to yield **48** (2.777 g, 86 %) as a white solid; mp 78 °C; $[\alpha]_D^{20}$ = –27.0 ° (c = 1.07, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 5.72 (dd, H-1), 2.78 (ddd, H-2), 1.73 (ddd, H-2'), 3.64 (m, H-3), 3.57 (dd, H-4), 4.22 (m, H-5), 3.73 (dd, H-6), 3.81 (dd, H-6'), 2.68 (s, 4H, imide), 0.09, 0.14, 0.15 (3s, 27H, Si-CH_3); $J_{1,2}$ = 7.0, $J_{1,2'}$ = 5.0, $J_{2,2'}$ = 13.7, $J_{2,3}$ = 4.5, $J_{2',3}$ = 5.5, $J_{3,4}$ = 6.0, $J_{4,5}$ = 6.0, $J_{5,6}$ = 4.1, $J_{5,6}$' = 5.6, $J_{6,6'}$ = 11.0; ^{13}C NMR ($CDCl_3$): δ = –7.32, –6.37, –6.64 (9C, Si-CH_3); 21.14 (2C, imide), 25.18 (C-2), 54.76 (C-6), 63.40, 64.40, 66.84 (C-3, C-4, C-5), 71.77 (C-1), 169.7 (2C, C=O-imide). Calcd for $C_{19}H_{39}NO_6Si_3$ (461.8): C, 49.42; H, 8.51; found: C, 49.15; H, 8.58.

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