197. The Allyl Ester as Carboxy-Protecting Group in the Stereoselective Construction of Neuraminic-Acid Glycosides

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The application of the allyl-ester moiety as protecting principle for the carboxy group of *N*-acetylneuraminic acid is described. Peracetylated allyl neuraminate **2** is synthesized by reacting the caesium salt of the acid **1** with allyl bromide. Treatment of **2** with HCl in AcCl or with HF/pyridine gives the corresponding 2-chloro or 2-fluoro derivatives **3** and **4**, respectively (*Scheme 1*). In the presence of Ag_2CO_3, the 2-chloro carbohydrate **3** reacts with di-*O*-isopropylidene-protected galactose **5** to give the 2–6 linked disaccharide with the α-D-anomer **6a** predominating (α-D/β-D = 6:1; *Scheme 2*). Upon activation of the 2-fluoro derivative **4** with $BF_3 \cdot Et_2O$, the β-D-anomer **6b** is formed preferentially (α-D/β-D = 1:5). In further glycosylations of **4** with long-chain alcohols, the β-D-anomers are formed exclusively (see **10** and **11**; *Scheme 4*). The allyl-ester moiety can be removed selectively and quantitatively from the neuraminyl derivatives and the neuraminyl disaccharides by Pd(0)-catalyzed allyl transfer to morpholine as the accepting nucleophile (see *Scheme 5*).

Introduction. – Sialic acids often terminate the oligosaccharide chains of glycolipids, glycoproteins, and gangliosides. They are involved in numerous biological processes, *e.g.* in the transport of potassium ions, amino acids, and viruses through membranes [1]. Due to their ionic character, sialic acids protect proteins from proteolytic attack. They also cause strong immunological effects since they often mask recognition structures of the glycoconjugates involved in cancer development [2], and may form the polymeric surface antigens of pathogenic bacteria [3]. Therefore, methods for the stereoselective construction of neuraminic-acid glycosides are of outstanding interest since they provide the tools for model studies of biological recognition processes and infections. For these purposes, the naturally occurring α-D-glycosides and also unnatural β-D-glycosides may be valuable targets.

The synthesis of neuraminyl glycosides is complicated by the presence of the carboxylic function adjacent to the anomeric C(2) of the polyfunctional aglycon. The corresponding 2-chloro and 2-bromo derivatives are subject to extensive elimination reactions under the conditions of glycoside synthesis and, therefore, the use of more stable glycosyl donors like, for instance, the 2-fluoro derivative might be a viable alternative[1]). Finally, the carboxylic acid usually is protected as the methyl ester which is cleavable only under basic conditions. However, for the construction of neuraminic acid containing *O*-glycopeptides, this protecting function is unsuitable due to the pronounced base sensitivity of these glycoconjugates [5].

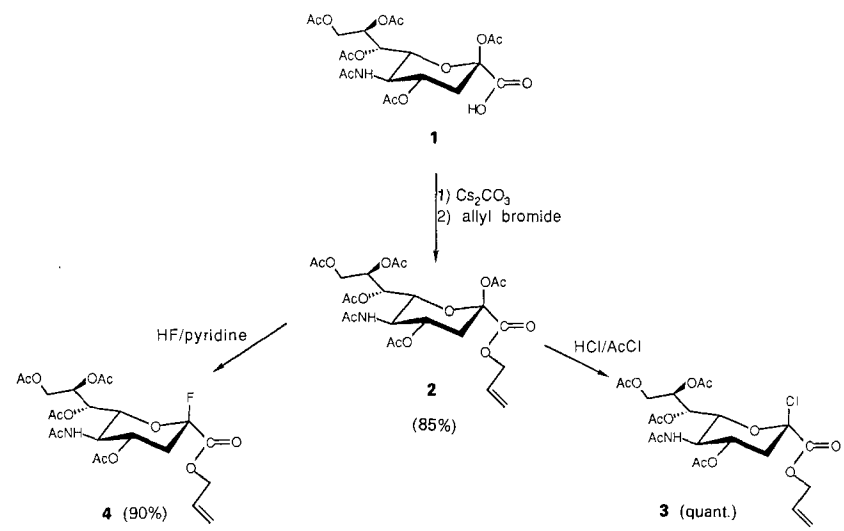
We have developed several protecting groups for glycopeptide synthesis [6]. In particular, we recently have described the allyl ester as protecting group for the construction

[1]) For glycosylations of *N*-acetylneuraminic acid based on the use of 2-chloro and 2-bromo derivatives, see *e.g.* [4].

both of *N*- and of base-labile *O*-glycopeptides [7] [8]. This paper reports on the use of the allyl ester as protecting function for the carboxy group of *N*-acetylneuraminic acid [9].

Results and Discussion. – The caesium salt of peracetylated neuraminic acid **1** was converted to the allyl ester **2** in high yield by treatment with allyl bromide *(Scheme 1)*. The rather unstable 2-chloro derivative **3** was formed by reaction of the ester **2** with HCl in AcCl. To minimize losses due to elimination of HCl, **3** was used without purification in the subsequent steps *(vide infra)*. By analogy to the corresponding methyl ester [4], **3** is suggested to be the β-D-isomer. Alternatively, treatment of **2** with HF/pyridine resulted in the formation of 2-deoxy-2-fluoroneuraminate **4** in excellent yield[2]). It is a crystalline compound and can be stored at −15° for several months without decomposition. Its configuration was determined by ^{19}F-NMR spectroscopy. The values for $J(F,H_{ax}–C(3)) = 33.8$ Hz and $J(F,H_{eq}–C(3)) = 6.6$ Hz proved the β-D-configuration. The stability of the allyl ester towards acids is illustrated by the fact that **4** was unaffected under acidic conditions.

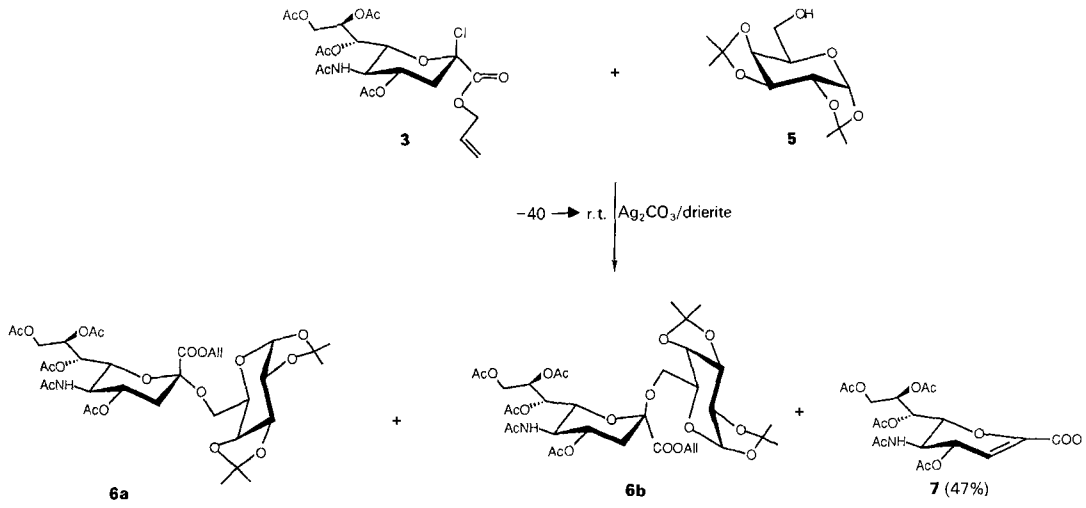
Scheme 1. *Synthesis of the Allyl 2-Chloro- and 2-Fluoro-2-deoxyneuraminate* **3** *and* **4**, *Respectively*



From the haloesters **3** and **4**, disaccharides can be built up stereoselectively. Thus, the chloro derivative **3** was treated with the acetal-protected galactose **5** in the presence of silver salts to yield a mixture **6a**/**6b** of the α-D- and β-D-anomer with the α-D-anomer **6a** predominating (α-D/β-D = 6:1; *Scheme 2*). The stereoisomers could not be separated by chromatography. In addition, extensive elimination of HCl from **3** leading to the by-product **7** could not be prevented. The α-D-anomer **6a** represents the terminal disaccharide unit of the glycans of glycophorin A, the major glycoprotein of human erythrocyte membranes B [1], and, in general, of the L-type glycoproteins [11].

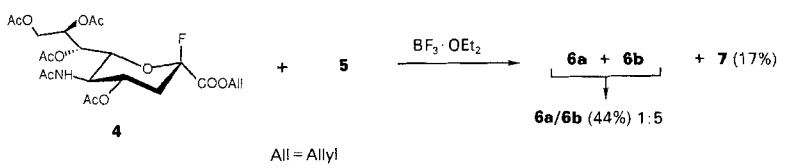
[2]) The analogous methyl ester has been described in [10].

Scheme 2. *Synthesis of the Neuraminosyl-galactoses* **6a** *and* **6b** *Using the Chloro Derivative* **3**



On the other hand, the 2-fluoro derivative **4** was activated by $BF_3 \cdot Et_2O$ in CH_2Cl_2 yielding preferentially the β-D-anomer **6b** (α-D/β-D = 1:5; *Scheme 3*). The elimination product **7** was also formed, however, to a much lesser extent (17%).

Scheme 3. *Synthesis of the Neuraminosyl-galactoses* **6a** *and* **6b** *Using the Fluoro Derivative* **4**

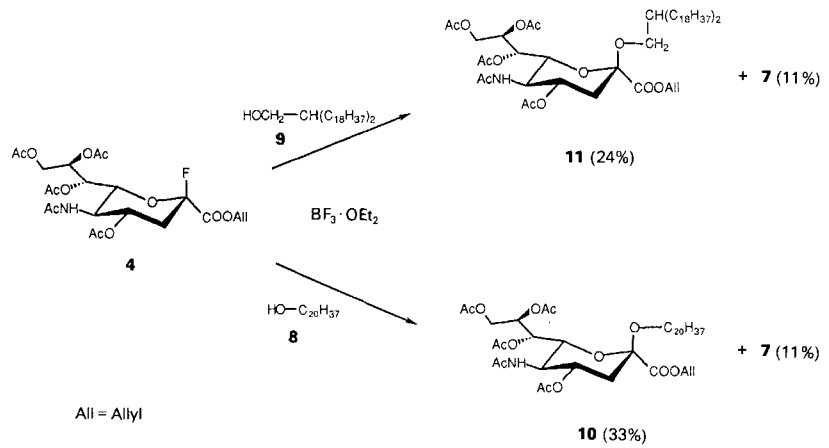


The structural assignments and the composition of the anomeric mixtures **6a**/**6b** were based on high field NMR spectra (in agreement with similar observations of *Paulsen et al.* and others [4], H–C(4) of the α-D-anomers of neuraminic-acid glycosides resonates at higher field (4.88 ppm) than H–C(4) of the β-D-anomer (5.44 ppm)).

The preference for β-D-anomer formation upon activation of **4** with $BF_3 \cdot Et_2O$ seems to be fairly general. As demonstrated in *Scheme 4*, the fluoro derivative **4** reacted with the long-chain alcohols **8** and **9** to yield exclusively the β-D-glycosides **10** and **11**. The latter two may be considered as model compounds for neuraminyl lipids being anchored in the cell membrane of pathogenic bacteria [3].

Finally, the allyl ester can be removed from neuraminic-acid derivatives by Pd(0)-catalyzed allyl transfer to morpholine as the accepting nucleophile [7] [8] without affecting the other protecting groups present. Thus, the peracetylated allyl neuraminate **2** was

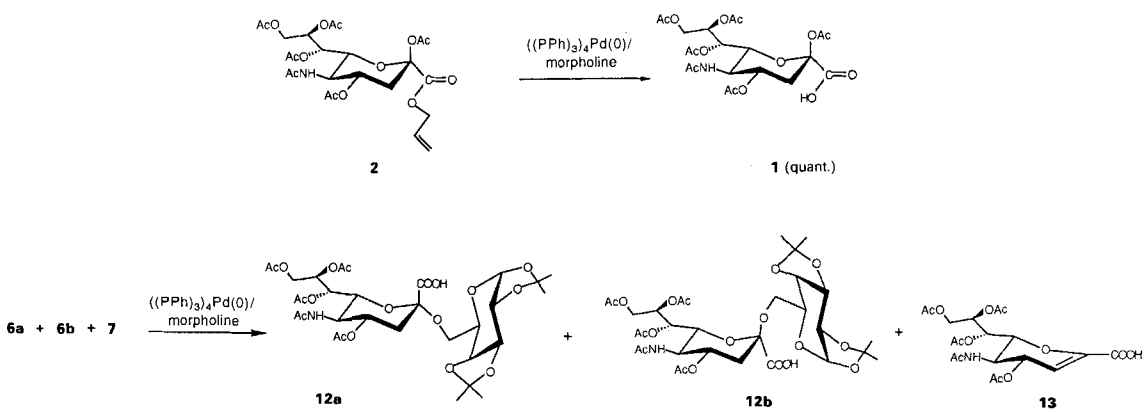
Scheme 4. *Synthesis of the Alkyl Neuraminosides* **10** *and* **11** *Using the Fluoro Derivative* **4**



treated with tetrakis(triphenylphosphine)palladium(0) in tetrahydrofurane/morpholine at room temperature for 30 min to yield the carboxy-deblocked acid **1** in quantitative yield and without any side reaction *(Scheme 5)*.

In order to get the glycosides **6a** and **6b** separated, the reaction mixture **6a**/**6b**/**7** was deallylated in the presence of the Pd(0) catalyst and morpholine in THF as the allylic acceptor, yielding after 2 h, the carboxy-deblocked compounds in 90% yield *(Scheme 5)*. However, this only resulted in a better separation of the elimination product **7** from the neuraminyl glycosides **6a**/**6b**.

Scheme 5. *Selective Cleavage of the Allyl Esters*



In conclusion, the allyl ester proves to be a valuable protecting group for the carboxylic-acid function of the biologically most important *N*-acetylneuraminic acid. It can be introduced very easily, is stable during the formation of the 2-chloro and 2-fluoro derivatives and glycosylation reactions, and can be removed quantitatively and selectively under almost neutral conditions.

Experimental Part

General. M.p.: uncorrected. Specific rotations: *Perkin Elmer 241*. IR spectra (in cm^{-1}): *Beckmann Acculab 2*. NMR spectra (δ in ppm rel. to TMS; J in Hz); *Bruker WH 270* (^1H, 270 MHz), *Bruker AM 400* (^1H, 400 MHz; ^{13}C, 100.13 MHz), *Bruker WP 80 DS* (^{13}C, 20.15 MHz), and *Bruker WH 90* (^{13}C, 22.63 MHz; ^{19}F, 84.67 MHz, fluorobenzene as internal standard). HR-MS of **7**: *Kratos MS 50*. FC = flash chromatography.

*Allyl 5-Acetamido-2,4,7,8,9-penta-*O*-acetyl-3,5-dideoxy-β-*D*-glycero-*D*-galacto-2-nonulopyranosonate* (**2**). To a soln. of 1.1 g (2.12 mmol) of peracetylated neuraminic acid **1** in 10 ml of EtOH, a soln. of 0.34 g (1.06 mmol) of caesium carbonate in 3 ml of H_2O was added. The resulting soln. was evaporated, the residue codistilled with benzene (3×), dried under reduced pressure, and taken up in 20 ml of freshly distilled DMF. Then, 12.8 g (0.1 mmol) of allyl bromide was added and the mixture stirred at r.t. for 24 h. The solvent was evaporated and the remaining residue purified by chromatography (petroleum ether/acetone 2:1) to yield 1 g (85%) of **2**. $[\alpha]_D^{22} = -30.4$ ($c = 0.3$, $CHCl_3$). IR (neat): 1740 (C=O, ester), 1650 (amide I). ^1H-NMR (270 MHz, $CDCl_3$): 5.88 (*ddt*, $J_{trans} = 17$, $J_{cis} = 10.4$, $J_{vic} = 5$, $CH{=}CH_2$); 5.42 (*d*, $J = 9.5$, NH); 5.37–5.2 (*m*, H–C(7), H–C(8); therein *dd* at 5.33 ($J_{trans} = 17$, $J_{gem} = 1.4$), H_{trans} of $CH{=}CH_2$, and *dd* at 5.23 ($J_{cis} = 10.4$), H_{cis} of $CH{=}CH_2$); 5.05 (*ddd*, H–C(4)); 4.65 (*m*, CH_2O); 4.44 (*dd*, $J(H_a{-}C(9), H_b{-}C(9)) = 12.4$, $J(H_a{-}C(9), H{-}C(8)) = 2.6$, $H_a{-}C(9)$); 4.16–4.08 (*m*, H–C(5), H–C(6), H_b–C(9)); 2.53 (*dd*, $J(H_{eq}{-}C(3), H{-}C(4)) = 5$, $J(H_{eq}{-}C(3), H_{ax}{-}C(3)) = 13.5$, H_{eq}–C(3)); 2.126, 2.12, 2.03, 2.013, 2.01 (5*s*, 5 CH_3CO); 1.87 (*s*, CH_3CONH). ^{13}C-NMR (20.15 MHz, (D_6)acetone): 171.7–169.9 (7 C=O); 132.6 ($CH{=}CH_2$); 118.5 ($CH{=}CH_2$); 98.5 (C(2)); 62.5 (C(9)); 49.3 (C(5)); 36.6 (C(3)); 22.9 (CH_3CONH); 20.8, 20.7, 20.5 (CH_3COO). Anal. calc. for $C_{24}H_{33}NO_{14}$: C 51.52, H 5.94, N 2.50; found: C 51.39, H 5.91, N 2.66.

*Allyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-2-chloro-2,3,5-trideoxy-β-*D*-glycero-*D*-galacto-2-nonulopyranosonate* (**3**). At 0°, 0.2 g (0.35 mmol) of **2** were suspended in 5 ml of a sat. soln. of HCl in AcCl. The mixture was stirred for 24 h while the temp. reached r.t. The volatils were evaporated, and the remaining residue was codistilled 3× with each, Et_2O and benzene, and dried: 0.19 g (quant.) of **3**. The product was used immediately for the subsequent glycosylation reactions.

*Allyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-2,3,5-trideoxy-2-fluoro-β-*D*-glycero-*D*-galacto-2-nonulopyranosonate* (**4**). At 0°, 0.6 g (1.07 mmol) of **2** were dissolved in 2.5 ml of a 65–70% soln. of HF in pyridine under N_2, and the soln. was stirred at 0° for 90 min. Then, 10 ml of ice-water and 90 ml of CH_2Cl_2 were added, the aq. layer was extracted 5× with 80 ml of CH_2Cl_2, the combined org. layer washed twice with brine, dried ($MgSO_4$), evaporated, and the residue crystallized on trituration with a little Et_2O to yield 0.5 g (90%) of **4**. M.p. 114–115°. $[\alpha]_D^{22} = -21.4$ ($c = 0.25$, $CHCl_3$). IR (KBr): 1740 (C=O, ester), 1650 (amide I). ^{19}F-NMR (84.67 MHz): 3.26 (*dd*, $J(F, H_{ax}{-}C(3)) = 33.82$, $J(F, H_{eq}{-}C(3)) = 6.62$). ^1H-NMR (400 MHz, (D_6)acetone): 5.95 (*ddt*, $J_{trans} = 17.4$, $J_{cis} = 10.2$, $J_{vic} = 5.4$, $CH{=}CH_2$); 5.45 (*dd*, $J(H{-}C(7), H{-}C(8)) = 6$, $J(H{-}C(7), H{-}C(6)) = 2.4$, H–C(7)); 5.4 (*dd*, $J_{trans} = 17.4$, $J_{gem} = 1$, H_{trans} of $CH{=}CH_2$); 5.35 (*dd*, $J_{cis} = 10.2$, $J_{gem} = 1$, H_{cis} of $CH{=}CH_2$); 5.29 (*d*, $J = 10.8$, NH); 5.2 (*m*, H–C(8)); 4.74 (*d*, $J = 5.4$, CH_2O); 4.31 (*dd*, $J(H_a{-}C(9), H_b{-}C(9)) = 12.6$, $J(H_a{-}C(9), H{-}C(8)) = 2.4$, H_a–C(9)); 4.3–4.22 (*m*, H–C(5), H–C(6)); 4.07 (*dd*, $J(H_b{-}C(9), H{-}C(8)) = 6$, H_b–C(9)); 2.54 (*ddd*, $J(H_{eq}{-}C(3), F) = 6.6$, $J(H_{eq}{-}C(3), H{-}C(4)) = 5.7$, $J(H_{eq}{-}C(3), H_{ax}{-}C(3)) = 13.8$, H_{eq}–C(3)); 2.23 (*ddd*, $J(H_{ax}{-}C(3), F) = 33.8$, $J(H_{ax}{-}C(3), H{-}C(4)) = 11.7$, H_{ax}–C(3)); 2.18, 2.14, 2.06, 2.04, 1.91 (5 CH_3CO). ^{13}C-NMR (22.63 MHz, (D_6)acetone): 170.6–169.7 (C=O); 132.4 ($CH{=}CH_2$); 118.9 ($CH{=}CH_2$); 108.7 (*d*, $J(C(2), F) = 237.6$, C(2)); 62.9 (C(9)); 34.6 (*d*, $J(C(3), F) = 30$, C(3)); 22.9 (CH_3CONH); 20.63 (CHCOO). Anal. calc. for $C_{22}H_{30}FNO_{12}$: C 50.86, H 5.82, N 2.70; found: C 50.64, H 5.81, N 2.68.

*6-*O*-(Allyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-*D*-glycero-*D*-galacto-2-nonulopyranosylonate)-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose* (**6a**), *6-*O*-(Allyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-β-*D*-glycero-*D*-galacto-2-nonulopyranosylonate)-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose* (**6b**), *and Allyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-2,6-anhydro-3,5-dideoxy-*D*-glycero-*D*-galacto-non-2-enopyranosonate* (**7**). *From Chloro Compound* **3**. Under reduced pressure, 0.53 g of Ag_2CO_3, 1.35 g of drierite, and 0.46 (1.79 mmol) of 1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose (**5**) were dried. Then 12 ml of CH_2Cl_2 were added, and, after stirring under N_2 for 1 h, the mixture was cooled to −45°. A soln. of 0.19 g (0.35 mmol) of **3** in 11 ml of CH_2Cl_2/toluene 1:1 was added dropwise. After stirring at −40° for 1 h, at −26° for 18 h, and at r.t. for 48 h, the mixture was filtered. The filtrate was washed twice with H_2O, dried ($MgSO_4$), and evaporated. The remaining residue was chromatographed twice on silica gel (petroleum ether/aceton 2.2:1) to yield 0.13 g (47%) of **6a**/**6b** 6:1 (by 400-MHz ^1H-NMR) and 0.08 g of **7**.

From Fluoro Compound **4**. *In vacuo*, 0.2 g (0.38 mmol) of **4**, 0.5 g (1.92 mmol) of **5**, and 2 g of powdered molecular sieve were dried. Then, 20 ml of CH_2Cl_2 were added, and the mixture was stirred at r.t. for 1 h. After dropwise addition of a soln. of 0.38 g (2.7 mmol) of $BF_3 \cdot Et_2O$ in 3 ml of CH_2Cl_2 and stirring at r.t. for 1 h, the

mixture was filtered. The filtrate was washed with H_2O, dried ($MgSO_4$), and evaporated. The residue was chromatographed as described above to yield 128 mg (44%) of **6a**/**6b** 1:5 and 33 mg (17%) of 7.

α-D-Anomer **6a**: ^{1}H-NMR (400 MHz, C_6D_6): 5.82 (*ddt*, CH=CH_2); 5.52 (*dd*, J(H–C(7′),H–C(8′)) = 7.2, J(H–C(7′),H–C(6′)) = 2.5, H–C(7′)); 5.51 (*d*, J(H–C(1),H–C(2)) = 5, H–C(1)); 5.25 (*dd*, J_{trans} = 17.2, J_{gem} = 1.2, H_{trans} of CH=CH_2); 5.08 (*dd*, J_{cis} = 10, J_{gem} = 1.2, J_{cis} of CH=CH_2); 4.88 (*ddd*, J(H–C(4′),H_{ax}–C(3′)) = 12.5, J(H–C(4′),H–C(5′)) = 10.2, J(H–C(4′),H_{eq}–C(3′)) = 4.9, H–C(4′)); 4.65 (*m*, OCH_2CH=CH_2); 4.43 (*dd*, J(H–C(3),H–C(4)) = 8.4, J(H–C(3),H–C(2)) = 2.5, H–C(3)); 2.85 (*dd*, J(H_{eq}–C(3′),H_{ax}–C(3′)) = 12.8, H_{eq}–C(3′)); 2.09, 1.92, 1.81, 1.55, 1.54 (5*s*, 5 CH_3CO); 1.49, 1.43, 1.16, 1.03 (4*s*, 4 CH_3–C). ^{13}C-NMR (100.6 MHz, C_6D_6): 118.8 (CH=CH_2); 109.3, 108.4 (2 $(CH_3)_2C$); 99.5 (C(2′)); 96.8 (C(1)); 49.4 (C(5′)).

β-D-Anomer **6b**: ^{1}H-NMR (400 MHz, C_6D_6): 5.45 (*d*, J(H–C(1),H–C(2)) = 5, H–C(1)); 5.4 (*ddd*, J(H–C(4′),H_{ax}–C(3′)) = 12, J(H–C(4′),H–C(5′)) = 10.2, J(H–C(4′),H_{eq}–C(3′)) = 4.9, H–C(4′)); 5.17 (*dd*, J_{trans} = 17.7, J_{gem} = 1.7, H_{trans} of CH=CH_2); 4.96 (*dd*, J_{cis} = 10, J_{gem} = 1.7, H_{cis} of CH=CH_2); 2.65 (*dd*, J(H_{eq}–C(3′),H_{ax}–C(3′)) = 12.8, H_{eq}–C(3′)); 1.95, 1.94, 1.73, 1.64, 1.63 (5*s*, 5 CH_3CO); 1.61, 1.54, 1.33, 1.06 (4*s*, 4 CH_3–C). ^{13}C-NMR (100.6 MHz, C_6D_6): 118.9 (CH=CH_2); 109.7, 108.5 (2 $(CH_3)_2C$); 99.7 (C(2′)); 96.8 (C(1)); 49.5 (C(5′)).

Elimination Product **7**: $[\alpha]_D^{22}$ = 41 (*c* = 0.23, $CHCl_3$). ^{1}H-NMR (400 MHz, C_6D_6): 6.14 (*d*, J(H–C(3),H–C(4)) = 2.7, H–C(3)); 5.78 (*ddt*, J_{trans} = 17.2, J_{cis} = 10.4, J_{gem} = 5.2, CH=CH_2); 5.7 (*dd*, J(H–C(7),H–C(6)) = 2.68, J(H–C(7),H–C(8)) = 3.46, H–C(7)); 5.65 (*m*, H–C(8)); 5.43 (*dd*, J(H–C(4),H–C(3)) = 2.71, J(H–C(4),H–C(5)) = 8.5, H–C(4)); 5.16 (*dd*, J(H–C(6),H–C(5)) = 12.3, J(H–C(6),H–C(7)) = 2.68, H–C(6)); 5.14 (*dd*, J_{trans} = 17.2, J_{gem} = 1.3, H_{trans} of CH=CH_2); 5.01 (*dd*, J_{cis} = 10.4, J_{gem} = 1.3, H_{cis}, CH=CH_2); 4.95 (*d*, *J* = 10, NH); 4.73 (*m*, H–C(5)); 4.56–4.45 (*m*, H–C(9), OCH_2CH=CH_2); 4.16 (*dd*, J(H_a–C(9),H_b–C(9)) = 10.1, J(H_b–C(9),H–C(8)) = 2.6, H_b–C(9)); 1.92, 1.85, 1.78, 1.67, 1.66 (5*s*, 5 CH_3CO). HR-MS (EI): 499.1694 (M^+, calc. 499.1690).

*Allyl (Cosyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-2,3,5-trideoxy-β-*D*-glycero-*D*-galacto-2-nonulopyranoside)-onate* (**10**). As described for **6a**/**6b**, 0.1 g (0.19 mmol) of **4** were reacted with 0.11 g (0.38 mmol) of icosanol (**8**) in the presence of 0.16 g (1.15 mmol) of $BF_3 \cdot Et_2O$. After FC (petroleum ether/acetone 4:1), 50 mg (33%) of **10** and 10.5 mg (11%) of 7 were obtained. **10**: $[\alpha]_D^{22}$ = −8 (*c* = 0.7, CH_2Cl_2). ^{1}H-NMR (400 MHz, C_6D_6): 5.75–5.67 (*m*, CH=CH_2, H–C(7), H–C(8)); 5.5–5.42 (*m*, H–C(6), H–C(4)); 5.1 (*dd*, J_{trans} = 17, J_{gem} = 1.1, H_{trans} of CH=CH_2); 4.96 (*dd*, J_{cis} = 10.3, J_{gem} = 1.1, H_{cis} of CH=CH_2); 4.62 (*d*, *J* = 10.2, NH); 4.5–4.35 (*m*, OCH_2CH=CH_2, H–C(9), H–C(5)); 4.1 (*dd*, J(H_a–C(9),H_b–C(9)) = 10.4, J(H_a–C(9),H–C(8)) = 1.9, H_a–C(9)); 3.9 (*dt*, J_{gem} = 6.3, J_{vic} = 9.5 Hz, H_a of OC$H_2$$CH_2$); 3.6 (*dt*, J_{gem} = 6.8, J_{vic} = 9.5, H_b of OC$H_2$$CH_2$); 2.61 (*dd*, J(H_{eq}–C(3), H_{ax}–C(3)) = 12.5, J(H_{eq}–C(3),H–C(4)) = 4.8, H_{eq}–C(3)); 2.02, 1.96, 1.78, 1.69, 1.67 (5*s*, CH_3CO); 1.45–1.35 (*m*, 16 CH_2); 1.0(*t*, *J* = 7.9, C$H_3$$CH_2$). Anal. calc. for $C_{42}H_{71}NO_{13}$: C 63.21, H 8.97, N 1.76; found: C 63.12, H 8.90, N 1.67.

*Allyl ((2-Octadecylcosyl) 5-acetamido-4,7,8,9-tetra-*O*-acetyl-2,3,5-trideoxy-β-*D*-glycero-*D*-galacto-2-nonulopyranoside)onate* (**11**). As described for **10**, 0.4 g (0.77 mmol) of **4**, 0.84 g (1.5 mmol) of octadecylicosanol (**9**), and 0.65 g (4.62 mmol) of $BF_3 \cdot Et_2O$ yielded, after FC (petroleum ether/acetone 4:1) 190 mg (24%) of **11** and 42 mg (11%) of 7. M.p. 33–34°. $[\alpha]_D^{22}$ = −10.6 (*c* = 0.72, CH_2Cl_2). ^{1}H-NMR (400 MHz, C_6D_6): 5.81–5.72 (*m*, CH=CH_2, H–C(7)); 5.66 (*ddd*, H–C(8)); 5.46–5.39 (*m*, H–C(6), H–C(4)); 5.16 (*dd*, J_{trans} = 17.2, J_{gem} = 1.4, H_{trans} of CH=CH_2); 5.03 (*dd*, J_{cis} = 10.4, J_{gem} = 1.4, H_{cis} of CH=CH_2); 4.90 (*d*, *J* = 10.4, NH); 4.54–4.41 (*m*, OCH_2CH=CH_2, H–C(9), H–C(5)); 4.21 (*dd*, J(H_a–C(9′),H_b–C(9′)) = 10.5, J(H_a–C(9′),H–C(8′)) = 2.3, H_a–C(9′)); 3.87 (*dd*, J_{vic} = 9.5, J_{gem} = 5.4, H_a of CH_2CH); 3.62 (*dd*, J_{vic} = 9.5, J_{gem} = 6.7, H_b of OCH_2CH); 2.63 (*dd*, J(H_{eq}–C(3),H_{ax}–C(3)) = 12.9, J(H_{eq}–C(3),H–C(4)) = 4.9, H_{eq}–C(3)); 2.02, 1.96, 1.8, 1.71, 1.66 (5*s*, CH_3CO); 1.6–1.3 (*m*, 69 H, CH($C_{17}H_{34}CH_3$)$_2$); 0.98 (2*t*, 2 CH_2CH_3). Anal. calc. for $C_{60}H_{107}NO_{13}$: C 68.60, H 10.27, N 1.33; found: C 68.88, H 10.50, N 1.51.

Selective Cleavage of the Allyl Ester. a) **1** *from the Monosaccharide* **2**. A soln. of 20 mg (35 μmol) of **2** in 2 ml of THF was stirred under Ar. Then, 3 mg (10 mol-%) of tetrakis(triphenylphosphine)palladium(0) and subsequently 100 mg (1.1 mmol, 32-fold excess) of morpholine were added, and the mixture was stirred at r.t. for 30 min. The volatiles were evaporated, and the remaining residue was chromatographed to yield 18 mg (quant.) of the selectively deblocked **1**.

b) **12a**/**12b** *from the Disaccharides* **6a**/**6b**. As reported for the cleavage of **2**, 100 mg of **6a**/**6b**/**7** yielded after 2 h, 80 mg of **12a**/**12b**/**13**. After FC (CH_2Cl_2/MeOH/AcOH 15:1:0.1), 70 mg of **12a**/**12b** were obtained.

*6-*O*-(5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α/β-*D*-glycero-*D*-galacto-2-nonulopyranosylonic acid)-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranoses* (**12a**/**12b**): ^{1}H-NMR (400 MHz, $CDCl_3$): 5.45 (*d*, J(H–C(1),H–C(2)) = 4.9, H–C(1)); 4.85 (*ddd*, J(H–C(4′),H_{ax}–C(3′)) = 11.3, H–C(4′)); 2.41 (*dd*, J(H_{eq}–C(3′), H_{ax}–C(3′) = 12.6, H_{eq}–C(3′)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 171.31, 171.16, 170.93, 170.40, 170.25 (5 CH_3CO); 109.48, 108.79 (2 $(CH_3)_2C$); 98.99 (C(2′)); 96.25 (C(1)).

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