DOI: 10.1002/ejoc.200500816

Synthesis of Saponins with Cholestanol, Cholesterol, and Friedelanol as Aglycones

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Keywords: Carbohydrates / Glycosylation / Glycosides / Immunostimulants / Saponins / Trichloroacetimidates

Procedures for the synthesis of branched Xylβ(1→3)[Galβ-(1→2)]-Glc and Xylβ(1→3)[Galβ(1→2)]-GlcUA trisaccharides β-linked to the 3-*O* of cholesterol, cholestanol, and friedelanol, respectively, were developed. To this end, β-selective glucosylation of cholesterol with glucosyl donors giving selective access to 2-*O*, 3-*O*, and 6-*O* was studied. This way intermediates **10** and **21** having 2-*O*-acyl, 3-*O*-benzyl and 4,6-*O*-benzylidene or also benzyl protection were obtained. Removal of the 2-*O*-acyl group and then galactosylation afforded β(1→2)-linked disaccharide intermediates **14** and **23**. Standard manipulations with the *O*-benzylidene and/or *O*-benzyl protecting groups gave selective access to the 3-*O* of the glucosyl residue, thus affording with a xylosyl donor the trisaccharide β-linked to the cholesteryl residue (compound **18**) as decisive intermediate. Also an alternative procedure to this compound via attachement of a Xylβ(1→3)Glc residue to cholesterol and then galactosylation could be developed. Total deprotection of **18** or regioselective introduction of a sulfate group and of a dodecylcarbamoyl residue at 6a-*O* furnished saponins **34**, **36**, and **38**, respectively. Hydrogenation of cholesteryl disaccharide **23** led directly to a 3a-*O*-unprotected cholestanyl disaccharide **39**. β-Selective xylosylation and transformation of the liberated glucose hydroxymethyl group into a carboxylic group afforded target molecule **1b** having the desired Xylβ(1→3)[Galβ(1→2)]-GlcUA β-linked to cholestanol. Similarly, a saponin analog was obtained having an α-linked L-rhamnosyl residue instead of the β-linked D-xylosyl residue. Application of the glycosylation sequence, as worked out for cholesterol, to friedelanol led to attachment of the Xylβ(1→3)[Galβ(1→2)]-Glc residue to the 3-*O* (compound **54**). Complete *O*-deacylation led to saponin **55**; oxidation of the hydroxymethyl group of the glucose residue to the carboxylic group and then deprotection afforded target molecule **2** containing the same trisaccharide residue as **1b**.

Introduction

Many microbial antigens stimulate the production of antibodies in a host, thus protecting against infectious diseases.[1] However, many antigens when used in vaccines exert only a weak effect on the immune system; therefore immune stimulants are required in order to elicit an appropriate immune response.[2] Combining such immunoadjuvants with synthetic antigens instead of antigens prepared from inactivated pathogens provides advantages over traditional vaccines, including improved clinical safety against contaminations with other pathogens and use of structurally well-defined and homogeneous antigens.[3,4] Typical adjuvants are Freund's complete and incomplete adjuvant (FCA and IFA), bacterial endotoxins, mineral salts (particularly aluminium-based mineral salts, i.e. alums) and saponins. Of particular interest are compounds which not only increase antigen persistence but have specific modulatory effects on the immune system, e.g. by enhancing antigen processing, and by creating a favourable cytokine environment in order to induce a potent humoral and cellular immune response. Saponins formulated as micelles with cholesterol and phospholipids e.g. ISCOMs (immuno stimulating complexes)[5] are such components.[5–8] Quillaja saponins are typically obtained by aqueous extraction from the cortex of the tree *Quillaja saponaria* Molina, a member of the Rosaceae family,[9] Their detergent[10–12] and biological properties[10–15] have been known for many years.

QS 21, an acylated bisdesmosidic triterpenoid saponin (Figure 1)[16,17] is a purified fraction of a Quillaja saponin extract that has been widely investigated as adjuvant. It was shown to enhance both humoral and cell-mediated immune responses in animals.[14] A number of clinical trials with QS 21 have been performed in patients with infectious diseases or cancer[18] and it appears as effective as an adjuvant for vaccines eliciting both antibodies and cytotoxic T cell responses.[18–20]

Structurally, QS 21 consists of a triterpene (quillaic acid) with two oligosaccharide chains attached (a branched trisaccharide and an unbranched tetrasaccharide) and a sugar containing a dimeric fatty acyl group which is linked to the reducing end sugar of the tetrasaccharide moiety, as shown in Figure 1.[18] The fatty acyl chains seem to play a critical role in immune stimulation, as derived from deacylated saponin DS-1 obtained via alkaline hydrolysis of saponin QS 21.[11,15,21,22] Strong alkaline hydrolysis of DS-1 yielded QS-

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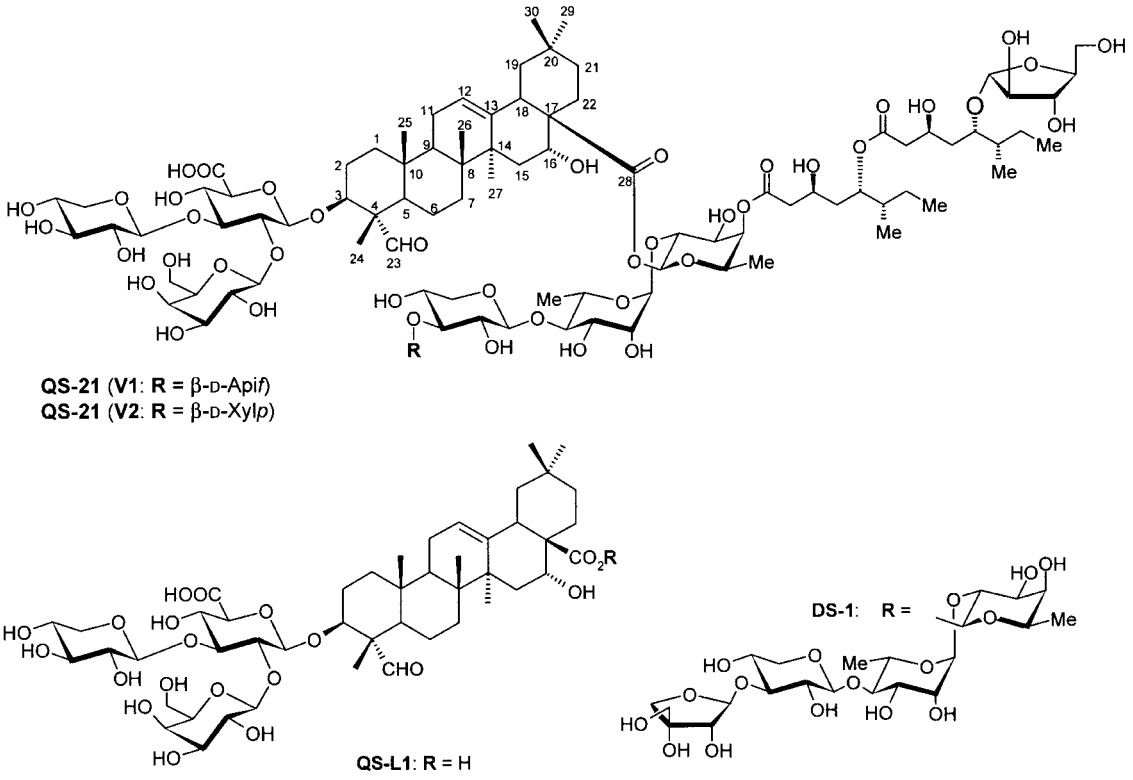


Figure 1. Structures of saponins QS-21, QS-L1, and DS-1.

L1.[10] This molecule was demonstrated to greatly increase both humoral immunity and cellular immune response when administered in the presence of alum-precipitated recombinant hepatitis B surface antigen.[23] However, when administered in the presence of the antigen alone, it showed low adjuvant efficacy.[23] Besides that, QS-L1 is also less toxic than QS 21 in vivo and in vitro, due to the lack of a lipophilic chain.[23] Hence, it is apparent that QS-L1 should use a distinct mechanism to stimulate immune response from the one used by QS-21. It is therefore of interest to synthesize analogs of QS-L1 in which the branched Xylβ(1→3)[Galβ(1→2)]GlcUA trisaccharide moiety is attached to cholestanol, cholesterol or friedelanol (for instance, compounds **1a**, **b**, **2** in Figure 2 or closely related derivatives), thus avoiding the use of the less accessible quillaic acid.[24,25] Because direct 3-*O*-glycosylation of triterpenes with a corresponding preprepared trisaccharide donor[26] did not lead to satisfactory anomeric selectivities,[24,27] as strategy the construction of the trisaccharide moiety after glucosylation of the desired aglycon was chosen.[24] This way, with the help of anchimeric assistance, better glycosylation results were expected. Success in this endeavour should also greatly facilitate the total synthesis of QS-21 and analogs.[28]

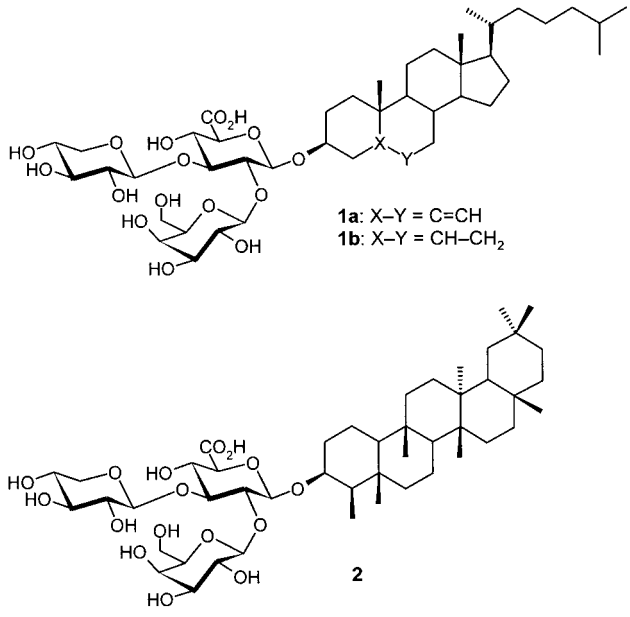


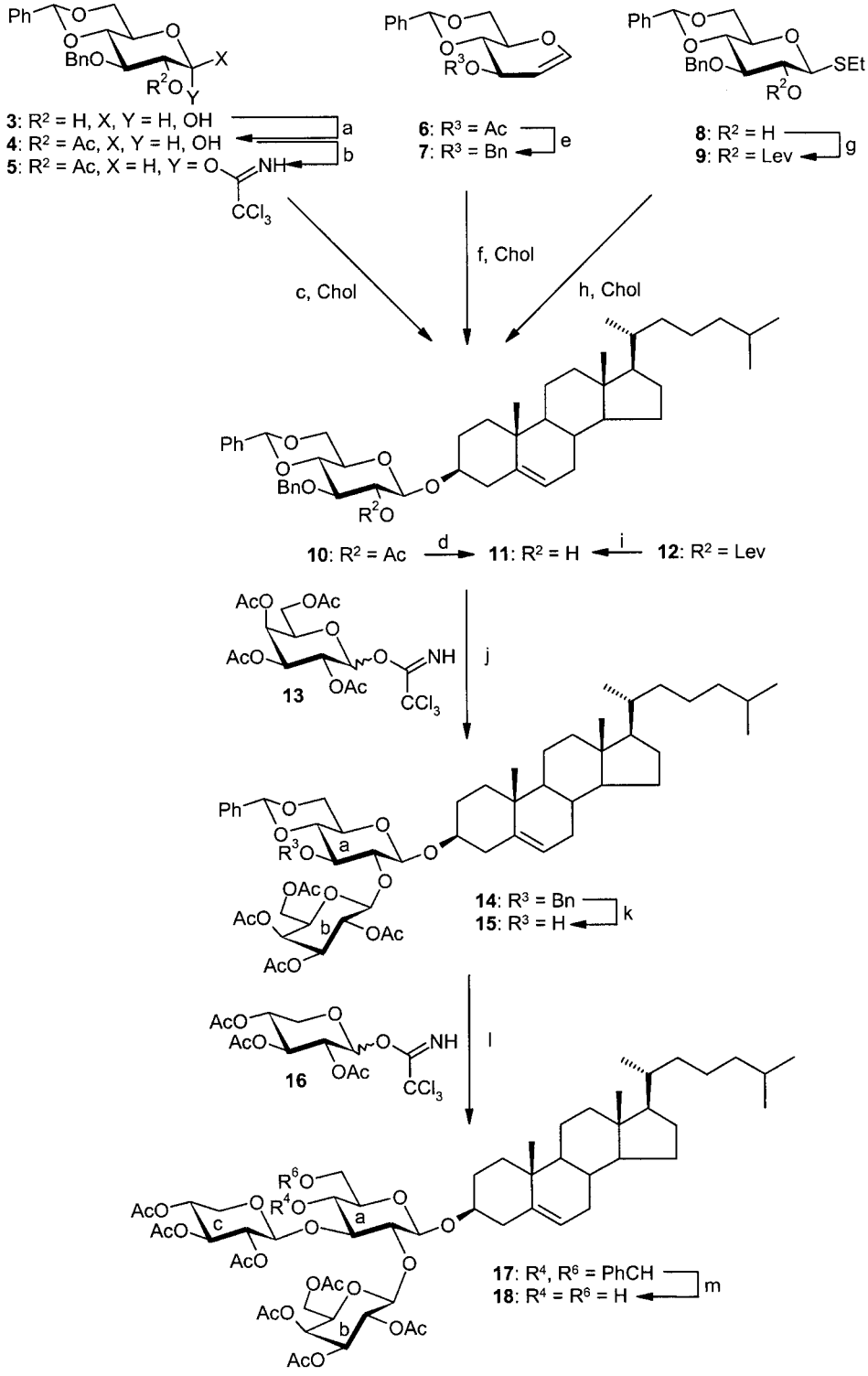
Figure 2. Structures of target molecules **1** and **2**.

Results and Discussion

Synthesis of Cholesterol- and Cholestanol-Based Saponins

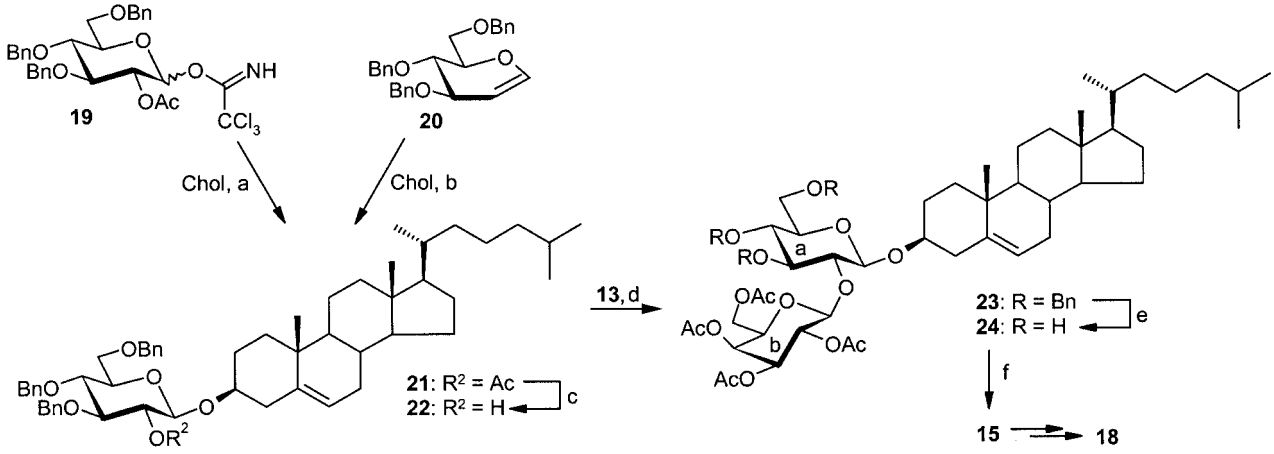
For the final attachment of the branched Xylβ(1→3)[Galβ(1→2)]GlcUA residue to the 3-*O* of steroids or terpenes a glucosyl donor was required which permitted access to 2-*O*, 3-*O*, and 6-*O* after the glycosylation step. To this end, the known 3-*O*-benzyl glucose[29] was transformed into 4,6-*O*-benzylidene derivative **3** (Scheme 1). Per-*O*-acetylation and chemoselective cleavage of the 1-*O*-acetyl group with hydrazinium acetate[30] afforded 1-*O*-unprotected compound **4** which gave with tri-

chloroacetonitrile in the presence of 1,8-diazabicylo[5.4.0]-undec-7-ene (DBU) as base trichloroacetimidate **5**.[31] Glycosylation of cholesterol (Chol) with **5** in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) as catalyst afforded β-glucopyranoside **10** in 40% yield. 2a-*O*-Deacetylation of **10** with sodium methoxide in methanol led quantitatively to 2a-*O*-unprotected **11** available for further chain extension. The modest glycosylation yield was reason

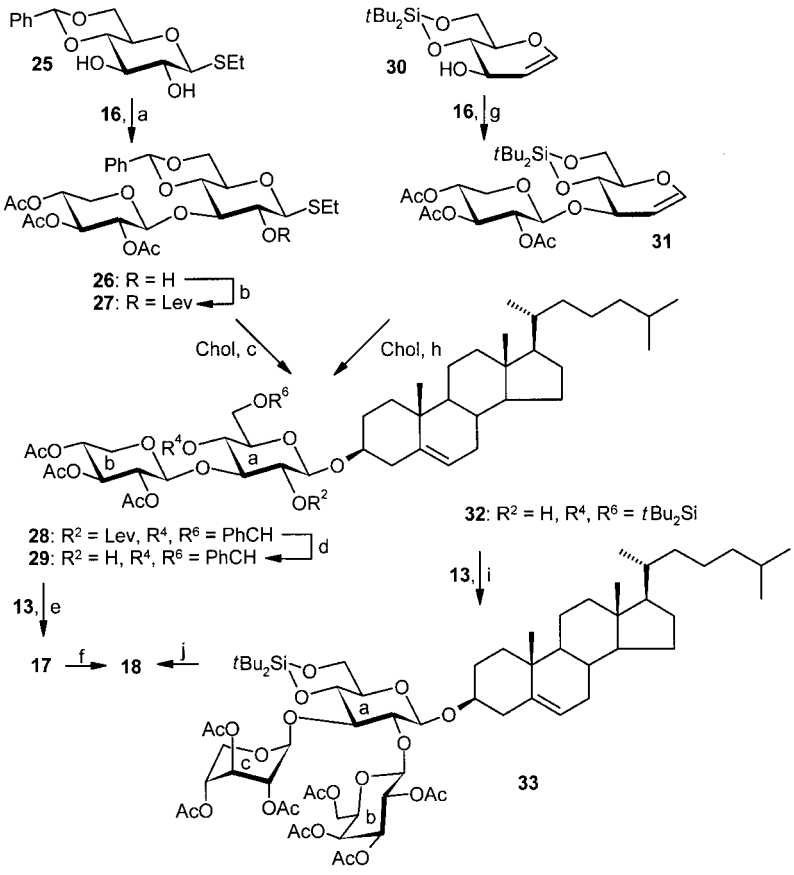


Scheme 1. Synthesis of cholesteryl saccharides **15** and **18**. Reagents and conditions: (a) Ac_2O, Pyr; N_2H_4·HOAc, DMF (51%); (b) CCl_3CN, DBU, CH_2Cl_2 (73%); (c) TMSOTf (0.05 equiv.), CH_2Cl_2 (41%); (d) NaOMe, MeOH/CH_2Cl_2 (qu); (e) NaOMe, MeOH; BnBr, NaH, DMF (51%); (f) DMDO, CH_2Cl_2; $ZnCl_2$, THF (13%); (g) LevOH, DCC, DMAP, CH_2Cl_2 (83%); (h) DMTST, 4-Å mol. sieves, CH_2Cl_2 (68%); (i) N_2H_4·HOAc, MeOH/CH_2Cl_2 (80%); (j) TMSOTf (0.05 equiv.), I. P., CH_2Cl_2 (69%); (k) Pd/C, H_2, EtOH/CH_2Cl_2 (22%); (l) TMSOTf (0.03 equiv.), CH_2Cl_2 (71%); (m) EtSH, TsOH, CH_2Cl_2 (86%).

to investigate other routes to **11**. To this end, the glycal assembly method[32] was probed. Hence, known glucal derivative **6**[33] was transformed into 3-*O*-benzyl derivative **7**; following treatment with dimethyldioxirane (DMDO) in order to generate the α-epoxide and then glycosylation of cholesterol in the presence of zinc chloride as Lewis acid gave **11** in only 13% yield. In a further approach to the synthesis of **11**, known thioglucoside **8**[34] was transformed into 2-*O*-levulinoyl (Lev) derivative **9** which gave with cholesterol in the presence of dimethyl(methylthio)sulfonium trifluorome-



Scheme 2. Synthesis of cholesteryl disaccharide **15**. Reagents and conditions: (a) TMSOTf (0.05 equiv.), CH_2Cl_2 (88%); (b) DMDO, CH_2Cl_2; $ZnCl_2$ THF (42%); (c) NaOH, MeOH/dioxane (qu); (d) TMSOTf (0.03 equiv.), IP, CH_2Cl_2, room temp. (76%); (e) Pd/C, H_2, EtOH/CH_2Cl_2 (qu) or $Pd(OH)_2$/C, H_2, EtOH/dioxane (92%); (f) Ph-CH(OMe)$_2$, CSA, MeCN (72%).



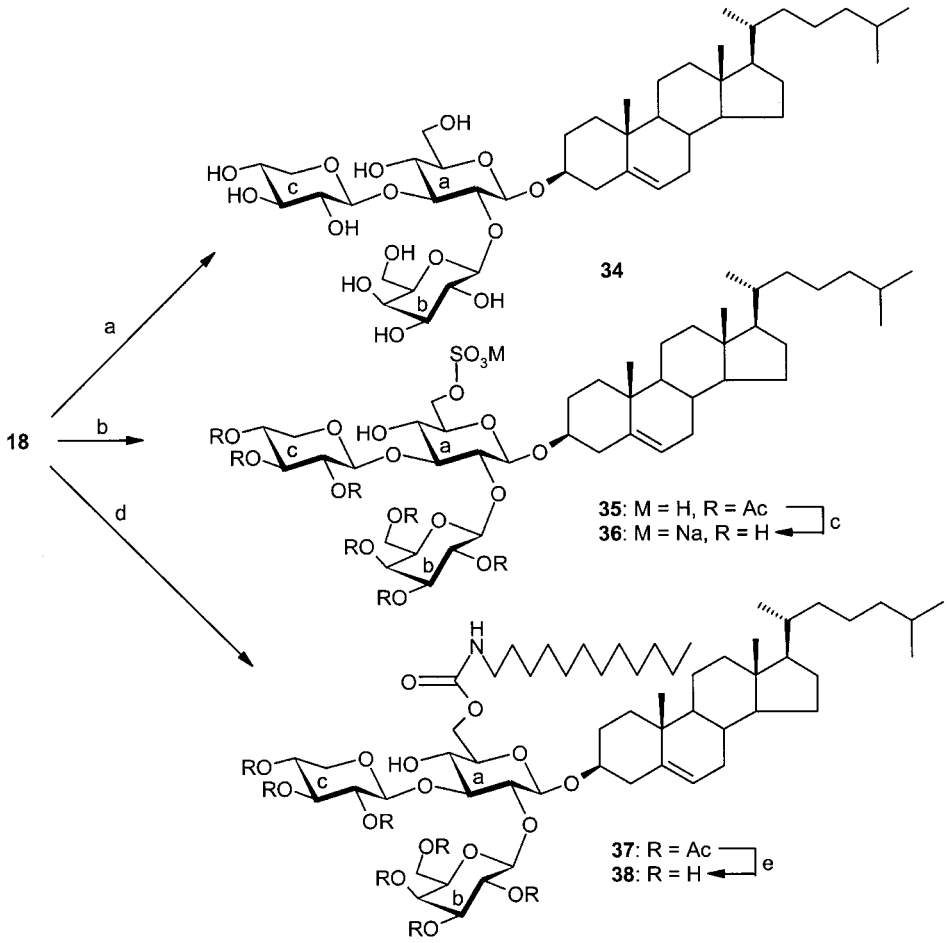
Scheme 3. Synthesis of cholesteryl trisaccharide **18** via a partially convergent route. Reagents and conditions: (a) TMSOTf (0.005 equiv.), 3-Å mol. sieves, IP, –75 → –65 °C, CH_2Cl_2 (86%); (b) Lev_2O, NEt_3, DMAP, CH_2Cl_2 (94%); (c) DMTST (3 equiv.), 4-Å mol. sieves, CH_2Cl_2, room temp. (74%); (d) N_2H_4·HOAc, MeOH/CH_2Cl_2 (64%); (e) TMSOTf (0.05 equiv.), IP, CH_2Cl_2, room temp. (64%); (f) see Scheme 1; (g) TMSOTf (0.001 equiv.), CH_2Cl_2, –70 → –45 °C (66%); (h) DMDO, CH_2Cl_2, 0 °C → room temp.; $ZnCl_2$, THF, –60 °C → room temp. (46%); (i) TMSOTf (0.03 equiv.), I. P., CH_2Cl_2, room temp. (91%); (j) HF·Pyr, THF (94%).

thanesulfonate (DMTST) as promoter the β-glucoside **12** in 68% yield. Cleavage of the levulinoyl group with hydrazinium acetate afforded **11** in 80% yield.

Glycosylation of acceptor **11** with the known galactosyl donor **13**[35] under TMSOTf catalysis afforded disaccharide **14** in 69% yield. Selective hydrogenolytic 3a-*O*-debenzylation of **14**, without affecting the cholesterol CC double bond and the benzylidene group could be carried out with palladium on carbon as catalyst, thus affording 3a-*O*-unprotected **15** though in only low yield. Glycosylation of **15** with known xylosyl donor **16**[36] went smoothly furnishing trisaccharide **17** in 71% yield, thus exhibiting that only some steps need improvement in this approach. Acid-catalyzed debenzylidenation with ethanethiol as nucleophile and *p*-toluenesulfonic acid (TsOH) as catalyst afforded the decisive intermediate **18**, useful for further group modifications.

In order to probe the influence of the 4a,6a-*O*-benzylidene group on the trisaccharide formation, the known glucosyl donor **19**,[37,38] having benzyl group protection at 4-*O* and 6-*O* was employed for the glucosylation of cholesterol providing glucoside **21** in 88% yield (Scheme 2). Basic cleavage of the 2a-*O*-acetyl group quantitatively furnished the 2a-*O*-unprotected derivative **22**. Glycal assembly between known tri-*O*-benzylglucal (**20**)[39] and cholesterol led to **22** in much lower yield. Galactosylation of **22** with **13** as galactosyl donor under application of the inverse procedure (IP)[40,41] (i.e., addition of the donor to a solution containing the acceptor and the TMSOTf catalyst) afforded disaccharide **23** in 76% yield. Hydrogenolysis with palladium on carbon or with Pearlman's catalyst afforded the desired 3a,4a,6a-*O*-unprotected disaccharide **24** in very high yield. Reaction with benzaldehyde dimethyl acetal in the presence of camphorsulfonic acid (CSA) as catalyst in acetonitrile installed the 4a-6a-*O*-benzylidene group to afford **15** in very high overall yield, thus giving easy access to intermediate **18**.

Some other alternatives for the synthesis of the decisive intermediate **18** were probed (Scheme 3). Regioselective glycosylation of known 2,3-*O*-unprotected glucose **25**[42] as acceptor with xylosyl donor **16** led under IP conditions at low temperature to 3-*O*-xylosylated disaccharide **26** in high yield. Introduction of a levulinoyl group at 2a-*O* (→ **27**) and then glycosylation of cholesterol furnished cholesteryl disaccharide **28** in 74% yield. Cleavage of the levulinoyl group (→ **29**) and then galactosylation with **13** as donor

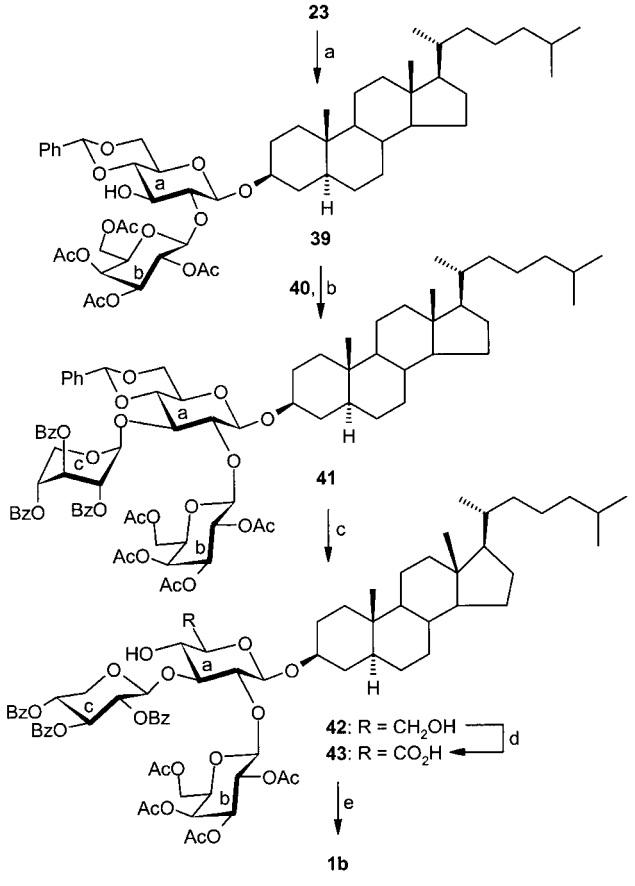


Scheme 4. Synthesis of unprotected cholesteryl trisaccharides **34**, **36**, and **38**. Reagents and conditions: (a) NaOMe, MeOH/CH_2Cl_2. IR-120 (H^+) (qu); (b) Pyr·SO_3, Pyr (35%); (c) NaOMe, MeOH/CH_2Cl_2. IR-120 (H^+). IR-120 (Na^+) (90%); (d) $Me(CH_2)_{11}NCO$, Pyr, 80 → 100 °C (84%); (e) NaOMe, MeOH/CH_2Cl_2; SiO_2, EE/MeOH/H_2O (9:5:2) (68%).

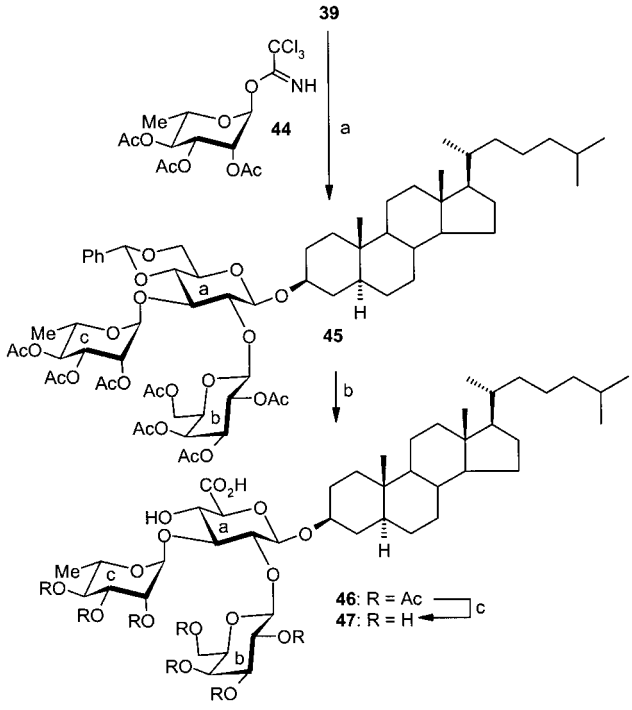
afforded under IP conditions cholesteryl trisaccharide **17** in 64% yield, which could be transformed into **18** as described above. Glycosylation of 4,6-*O*-di-*tert*-butylsilanediyl-protected glucal **30**[43] with xylosyl donor **16** at low temperature afforded the acid-sensitive disaccharide **31** in 66% yield. However, glycal assembly of this compound with cholesterol afforded cholesteryl disaccharide **32** in only modest yield. Glycosylation of **32** with xylosyl donor **13** under IP conditions afforded trisaccharide **33** in excellent yield. Presumably due to the presence of the bulky di-*tert*-butylsilanediyl protection of the glucopyranosyl residue, the xylopyranosyl residue prefers to be in $^1C_4$-conformation as indicated be the ^{1}H NMR spectroscopic data ($J_{1c,2c} \approx J_{3c,4c} \approx 0$ Hz). Cleavage of the silanediyl group with the HF-pyridine complex in THF afforded in high yield compound **18** in which the xylopyranosyl residue prefers the $^4C_1$-conformation ($J_{1c,2c} = 6.7$, $J_{2c,3c} \approx J_{3c,4c} = 8.6$ Hz).

With these high yielding routes to the decisive intermediate **18** in hand, some target molecules were readily available. Cleavage of *O*-acyl protecting groups with sodium methoxide in methanol led to unprotected compound **34** (Scheme 4). Treatment of **18** with the sulfur trioxide–pyridine complex in pyridine regioselectively led to the 6a-*O*-sulfated intermediate **35**. *O*-Deacylation under standard conditions and then transformation into the sodium salt with sodium loaded ion exchange resin IR-120 furnished sulfate **36**. Finally, because synthetic modifications of QS-21 having an *N*-dodecylamide residue at C-6a exhibited interesting biological properties,[21,44] carbamate derivative **37** was prepared by treatment of **18** with *N*-dodecyl isocyanate in pyridine. *O*-Deacetylation and then chromatographic purification afforded the desired 6a-*O*-carbamoylated **38** in 68% yield.

The synthesis of target molecule **1b** started from intermediate **23** (Scheme 5), which was readily obtained from cholesterol and glycosyl donors **19** and **13** (see Scheme 2). Hydrogenation of **23** in the presence of acetic acid/formic acid in EtOH/CH_2Cl_2 led to loss of the benzylidene group and hydrogenation of the cholesterol CC double bond.[45] The cholestane derivative obtained was immediately transformed into the 4a,6a-*O*-benzylidene derivative **39** by treatment with benzyldehyde dimethyl acetal in the presence of *p*-toluenesulfonic acid as catalyst in acetonitrile. Glycosylation of **39** with *O*-benzoyl-protected xylopyranosyl donor **40**[46] under TMSOTf catalysis afforded trisaccharide **41** in 75% yield; the xylopyranosyl residue again preferentially adopted a $^1C_4$-conformation ($J_{1c,2c} \approx J_{2c,3c} = 3.0$ Hz; $J_{3c,4c} = 3.3$ Hz). Hydrogenolytic or acid-catalyzed debenzylidenation afforded 4a,6a-*O*-unprotected cholestanyl trisaccharide **42**. Oxidation of the hydroxymethyl group of the glucose residue to the carboxylate group was performed with



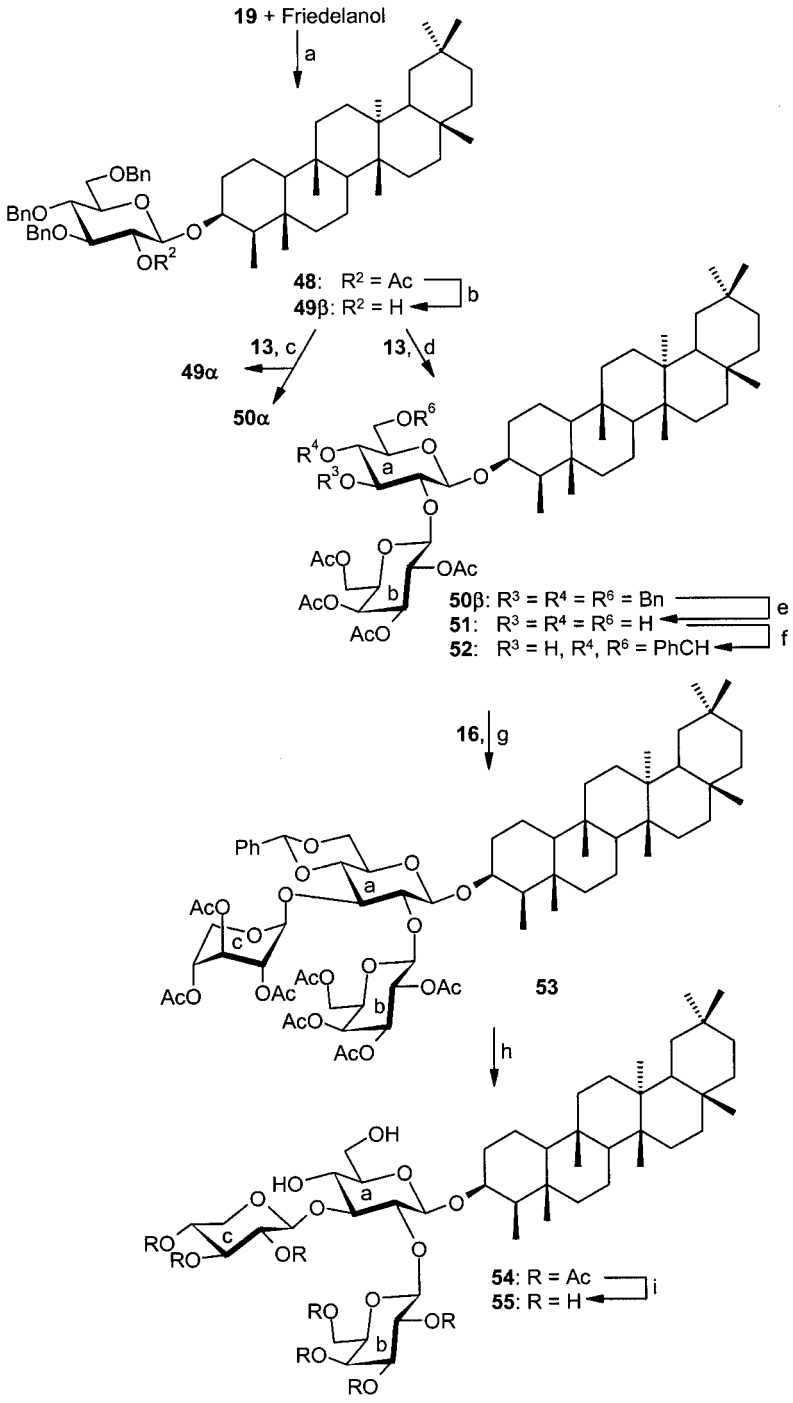
Scheme 5. Synthesis of target molecule **1b**. Reagents and conditions: (a) Pd/C, H_2, HOAc/HCO_2H, EtOH/CH_2Cl_2; Ph-$CH(OMe)_2$, TsOH, MeCN (76%); (b) TMSOTf (0.01 equiv.), CH_2Cl_2 (75%); (c) $Pd(OH)_2$/C, H_2, HOAc, EtOH/dioxane (67%) or EtSH, TsOH, CH_2Cl_2 (88%); (d) TEMPO, NaOCl, TBABr, NaCl, CH_2Cl_2/H_2O/$NaHCO_3$ (68%); (e) NaOMe, MeOH; IE: IR 120 (H^+); SiO_2, $CHCl_3$/MeOH/H_2O (60:35:8) (45%).



Scheme 6. Synthesis of structural analog **47**. Reagents and conditions: (a) TMSOTf (0.01 equiv.), CH_2Cl_2 (94%); (b) EtSH, TsOH, CH_2Cl_2 (88%); TEMPO, NaOCl, TBACl, KBr, CH_2Cl_2, NaOH, $NaHCO_3$ (73%); (c) NaOMe, MeOH/CH_2Cl_2. IR-120 (H^+) (95%).

tetramethylpiperidineoxyl (TEMPO) and sodium hypochlorite as oxidizing agent in the presence of tetrabutylammonium bromide in a two-phase system, thus furnishing the glucuronic acid (GlcUA) containing trisaccharide **43**. *O*-Deacylation under standard conditions and ion exchange with IR-120 (H^+-form) afforded target molecule **1b**.

In quillaja saponins the Rhaα(1→3)[Galβ(1→2)]GlcUA motif is also found.[47,48] Therefore, similarly 4a,6a-*O*-unprotected intermediate **39** was treated with the known rhamnosyl donor **44**[49] in the presence of TMSOTf as catalyst to furnish cholestanyl trisaccharide **45** in very high yield (Scheme 6). Acid-catalyzed debenzylidenation and then oxidation of the hydroxymethyl group as described above led to compound **46** having the glucuronate moiety installed. *O*-Deacetylation and ion exchange as described led to unprotected **47** which is structurally closely related to **1b**.

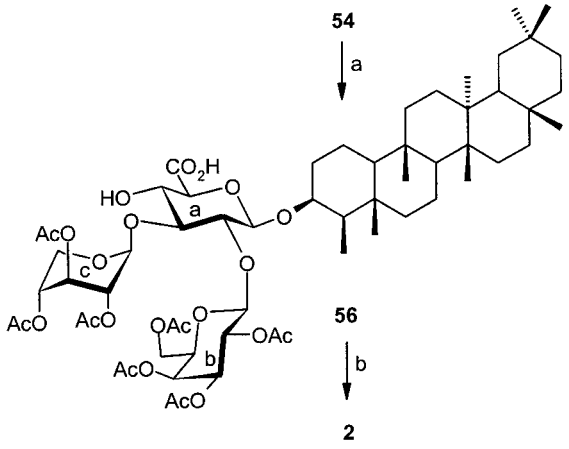


Scheme 7. Synthesis of friedelanyl trisaccharide **55**. Reagents and conditions: (a) TMSOTf (0.16 equiv.), CH_2Cl_2, room temp. (54%); (b) NaOMe, MeOH, CH_2Cl_2 (84%); (c) TMSOTf (0.03 equiv.), IP, CH_2Cl_2 (37%, **49α/50α** = 1:2); (d) TMSOTf (0.03 equiv.), CH_2Cl_2, room temp. (78%); (e) Pd/C, H_2, MeOH/CH_2Cl_2 (95%); (f) $PhCH(OMe)_2$, TsOH, MeCN (92%); (g) TMSOTf (0.03 equiv.), CH_2Cl_2, room temp. (94%); (h) EtSH, TsOH, CH_2Cl_2 (60%); (i) NaOMe, MeOH/CH_2Cl_2 (qu).

Synthesis of Friedelanol-Based Saponins

Extension of these results to the triterpenoid friedelanol as aglycon could be readily performed (Scheme 7). Glycosylation of friedelanol with glucosyl donor **19**[38,38] in the presence of TMSOTf as catalyst afforded the glucopyranoside **48** in 54% yield; 2a-*O*-deacetylation under standard conditions gave 2a-*O*-unprotected intermediate **49β**. Glycosylation of **49β** with galactosyl donor employing the inverse procedure (IP) afforded besides the anomerized **49α** ($J_{1a,2a}$ = 4.0 Hz) also the corresponding 2a-*O*-galactosylated product **50α** ($J_{1a,2a}$ = 4.0, $J_{1b,2b}$ = 8.0 Hz). In order to avoid acid-catalyzed anomerisation of **49β** during the glycosylation process favoured by IP, which is presumably due to the presence of the sterically demanding methyl groups at *C*-4 and *C*-5 of the friedelanol residue, the reaction of **49β** with donor **13** was carried out with TMSOTf as catalyst employing the normal procedure; thus, the β-linked friedelanyl-disaccharide **50β** was obtained in 78% yield. The hydrogenolytic *O*-debenzylidenation with palladium on carbon as catalyst afforded the 3a,4a,6a-*O*-unprotected intermediate **51**. Regioselective introduction of the 4a,6a-*O*-benzylidene protecting group could be readily performed with benzaldehyde dimethyl acetal under *p*-toluenesulfonic acid catalysis leading to compound **52** having the 3a-*O*-unprotected. Xylosylation of **52** with donor **16**[36] under TMSOTf catalysis afforded the friedelanol trisaccharide **53** in 93% yield. Acid-catalyzed debenzylidenation with ethanethiol as nucleophile (→ **54**) and then *O*-deacetylation furnished target molecule **55** in very high overall yield.

Synthesis of the target molecule **2** could be accomplished starting from the readily accessible intermediate **54** (Scheme 8). Oxidation of the hydroxymethyl group of the glucose residue as described above furnished compound **56** which contained the desired glucuronate residue. Based on the ^{1}H NMR spectroscopic data of **56** the xylopyranosyl residue seems to equilibrate between the $^1C_4$ and the $^4C_1$-conformation ($J_{1c,2c}$ = 4.5, $J_{2c,3c}$ = 6.6 Hz). *O*-Deacetylation of **56** and treatment with ion exchange resin IR-120 (H^+-form) furnished target molecule **2**.



Scheme 8. Synthesis of target molecule **2**. Reagents and conditions: (a) TEMPO, NaOCl, TBAB, NaBr, CH_2Cl_2, H_2O, $NaHCO_3$ (76%); (b) NaOMe, MeOH. IR-120 (H^+) (62%).

Conclusions

The construction of branched cholesteryl, cholestanyl, and friedelanyl trisaccharide saponin glycosides containing β-linked glucopyranosyl or glucuronopyranosyl, galactopyranosyl, and xylopyranosyl residues could be readily accomplished in a stepwise fashion. Very good results were obtained by β-glucosylation of cholesterol and friedelanol, then β-galacosylation at 2-*O* and β-xylosylation at 3-*O* of the glucosyl residue and finally oxidation of the glucose hydroxymethyl group leading to the glucuronate. These results should provide a valuable entry to the synthesis of more complex analogs of saponins QS L1 and finally to the synthesis of QS 21.

Experimental Section

Solvents were purified according to standard procedures. NMR spectra were recorded at 22 °C on a Bruker AC 250 Cryospec or Bruker DRX 600 spectrometer. Tetramethylsilane (TMS) or the resonance of the deuterated solvent was used as internal standard; solvent: $CDCl_3$, δ = 7.24; D_2O, δ = 4.63; [D_6]DMSO, δ = 2.49 ppm. MALDI mass spectra were recorded on a Kratos Kompact Maldi 2 spectrometer and 2,5-dihydroxybenzoic acid (DHB) was used as matrix. FAB MS spectra were obtained with a Finnigan MAT 312/AMD 5000 instrument; +6 kV for positive ions, –4 kV for negative ions. Thin-layer chromatography was performed on Merck 60 F_{254} silica gel plastic plates or Merck RP-18 glass plates; compounds were visualized by treatment with a solution of [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] (20 g) and $Ce(SO_4)_2$ (0.4 g) in 10% sulfuric acid (400 mL). Flash chromatography was performed on J. T. Baker silica gel 60 (40–63 μm) at a pressure of 0.3 bar. Optical rotations were measured at 25 °C with a Perkin–Elmer 241/MS polarimeter at the sodium D line.

3-*O*-Benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranose (3): 3-*O*-Benzylglucose[33] **6** (1.7 g, 6.30 mmol) was dissolved in acetonitrile (50 mL). To the well-stirred solution were added benzaldehyde dimethyl acetal (1.1 mL, 7.5 mmol) and *p*-toluenesulfonic acid (20 mg, 0.126 mmol, 0.02 equiv.). After complete conversion (TLC control, PE/EtOAc, 1:1) the mixture was neutralized with triethylamine, evaporated and purified by column chromatography (SiO_2, 60 g, petroleum ether/ethyl acetate, 2:1 → 1:1) to give the benzylidene compound **3** (1.5 g, 4.19 mmol, 76%). R_f(α,β-mixture) = 0.31/0.40 (petroleum ether/ethyl acetate, 1:1). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 2.50 (d, $^3J_{OH,2\alpha}$ = 5.7 Hz, 0.6 H, 2α-OH), 2.70 (s, 0.4 H, 1β-OH), 3.19 (d, $^3J_{OH,1\alpha}$ = 3.0 Hz, 0.6 H, 1α-OH), 3.45–5.00 (m, 8.4 H, 1β-, 2-, 3-, 4-, 5-, 6-H_a, 6-H_b, CH_2Ph), 5.27 (dd, $^3J_{1\alpha,OH}$ = $^3J_{1\alpha,2}$ = 3.0 Hz, 0.6 H, 1α-H), 5.56 (s, 1 H, PhCH), 7.22–7.51 (m, 10 H, 2 Ph). MALDI-MS (positive Mode, Matrix DHB, THF): 380.8 [*M* + Na]$^+$, 396.9 [*M* + K]$^+$. $C_{20}H_{22}O_6\cdot 0.25H_2O$ (362.8): calcd. C 66.20, H 6.24; found C 66.26, H 6.00.

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranose (4): A solution of the benzylideneglucose **3** (1.3 g, 3.60 mmol) in pyridine (20 mL) and acetic anhydride (10 mL) was stirred at room temp. for 5 h (TLC product: R_f = 0.73, PE/EtOAc, 3:1). Then the solution was concentrated in vacuo and codistilled several times with toluene. The residue was dissolved in DMF (18 mL) and treated with hydrazinium acetate (400 mg, 4.36 mmol). The mixture was stirred vigorously at 30–40 °C for 45 min. Then, the reaction was diluted with ethyl acetate (100 mL) and extracted with brine (3 × 10 mL). The organic layer was dried (magnesium sulfate) and

evaporated, the residue purified by flash chromatography (SiO_2, 60 g, petroleum ether/ethyl acetate, 3:1) to give compound **4** (740 mg, 1.85 mmol, 51% over 2 steps). R_f(α,β-mixture) = 0.38/0.425 (petroleum ether/ethyl acetate, 3:1). R_f(α,β-mixture) = 0.11/0.19 (toluene/acetone, 5:1). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 2.05, 2.07 (2s, 3 H, α,β-CH_3CO), 3.41–4.14 (m, 4 H, 3-, 4-, 5-, 6-H_a), 4.24–4.39 (m, 1 H, 6-H_b), 4.64–4.91 (m, 3.4 H, 1β-, 2-H, CH_2Ph), 5.40 (dd, $^3J_{1,OH}$ = 0, $^3J_{1,2}$ = 3.7 Hz, 0.6 H, 1α-H), 5.56–5.58 (2s, 1 H, α,β-PhCH), 7.14–7.51 (m, 10 H, 2 Ph). $C_{22}H_{24}O_7$ (400.4): calcd. C 65.99, H 6.04; found C 66.02, H 6.01.

***O*-(2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl) Trichloracetimidate (5):** To a solution of **4** (500 mg, 1.25 mmol) in dichloromethane (10 mL) were added trichloracetonitrile (700 μL, 7.00 mmol) and 3 drops of DBU. The reaction mixture was stirred at room temp. for 1 h. The solution was concentrated in vacuo and separated by flash chromatography (SiO_2, 4×5, petroleum ether/ethyl acetate, 3:1 + 0.5% NEt_3) to give the imidate **5** (500 mg, 0.92 mmol, 73%). R_f = 0.55 (petroleum ether/ethyl acetate, 3:1). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 1.98 (s, 3 H, CH_3CO), 3.79 (m, 2 H, 3-, 4-H), 3.99–4.12 (m, 2 H, 5-, 6-H_a), 4.33 (dd, $^2J_{6\text{-}Hb,6\text{-}Ha}$ = 10.3, $^3J_{6\text{-}Hb,5}$ = 4.8 Hz, 1 H, 6-H_b), 4.73–4.92 (2d, ^2J = 11.8 Hz, 2 H, CH_2Ph), 5.07 (dd, $^3J_{2,1}$ = 3.8, $^3J_{2,3}$ = 9.6 Hz, 1 H, 2-H), 5.60 (s, 1 H, PhCH), 6.49 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 7.24–7.51 (m, 10 H, 2 Ph), 8.59 (s, 1 H, NH). FAB-MS (positive Mode, Matrix NBA + NaI, THF): 568 [M + Na]$^+$. $C_{24}H_{24}Cl_3NO_7$ (544.8): calcd. C 52.91, H 4.44, N 2.56; found C 52.95, H 4.45, N 2.11.

1,5-Anhydro-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-*arabino*-hex-1-enitol (7): The acetylated glucal **6**[33] (50 mg, 0.181 mmol) was dissolved in methanol (2 mL) and treated with sodium methoxide (1 mg, 0.018 mmol) overnight. Deacetylation was complete (TLC: R_f = 0.55, PE/EtOAc, 2:1) and the solvent was evaporated. The residue was redissolved in DMF (3 mL) and benzyl bromide (60 μL, 0.50 mmol) followed by sodium hydride (25 mg, 1.0 mmol) were added. TLC (PE/EtOAc, 3:1) indicated total consumption of the starting material. Methanol (0.2 mL) was added to destroy the excess of sodium hydride. The mixture was diluted with diethyl ether and washed with saturated NaCl solution. Evaporation and purification by flash chromatography (SiO_2, 3×11, PE/EtOAc, 10:1) afforded the benzylated glucal **7** (30 mg, 0.093 mmol, 51% over 2 steps). R_f(product) = 0.72 (petroleum ether/ethyl acetate, 3:1). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 3.78–4.05 (m, 3 H, 4-, 5-H, 6-H_a), 4.32–4.38 (m, 2 H, 3-H, 6-H_b), 4.67–4.83 (m, 3 H, 2-H, CH_2Ph), 5.62 (s, 1 H, PhCH), 6.33 (d, $^3J_{1,2}$ = 6.2 Hz, 1 H, 1-H), 7.24–7.48 (m, 10 H, 2 Ph). Analytical data are in accordance with the literature.[50]

Ethyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-levulinoyl-1-thio-β-D-glucopyranoside (9): A stirred solution of compound **8**[34] (320 mg, 0.796 mmol), levulinic acid (230 mg, 2.0 mmol) and *N*,*N*-dicyclohexylcarbodiimide (DCC) (206 mg, 1.0 mmol) in CH_2Cl_2 (15 mL) was activated by 4-(dimethylamino)pyridine (DMAP) (10 mg, 0.08 mmol). Stirring was continued overnight. After complete protection (TLC: PE/EtOAc, 3:1) the precipitated urea was filtered off and the filtrate was washed with saturated $NaHCO_3$ solution. The CH_2Cl_2 layer was concentrated and purified by column chromatography (SiO_2, 80 g, petroleum ether/ethyl acetate, 3:1 → 2:1) to give the levulinoylated compound **9** (330 mg, 0.660 mmol, 83%). R_f(product) = 0.46 (petroleum ether/ethyl acetate, 3:1). R_f(starting material) = 0.52 (petroleum ether/ethyl acetate, 3:1). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 1.23 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.16 (s, 3 H, $H_3CCOCH_2CH_2CO$), 2.53 (t, ^3J = 6.5 Hz, 2 H, $H_3CCOCH_2CH_2CO$), 2.60–2.77 (m, 4 H, SCH_2CH_3, $H_3CCOCH_2CH_2CO$), 3.42–3.51 (m, 1 H, 5-H), 3.69–3.80 (m, 3 H, 3-, 4-H, 6-H_a), 4.32–4.38 (dd, $^2J_{6\text{-}Hb,6\text{-}Ha}$ = 10.5, $^3J_{6\text{-}Hb,5}$ = 6.9 Hz, 1 H, 6-H_b), 4.44 (d, $^3J_{1,2}$ = 10.1 Hz, 1 H, 1-H), 4.67–4.87 (2d, ^3J = 11.9 Hz, 2 H, CH_2Ph), 5.00–5.07 (ddd, $^3J_{2,1}$ = $^3J_{2,3}$ = 10.1, $^4J_{2,4}$ = 2.5 Hz, 1 H, 2-H), 5.56 (s, 1 H, PhCH), 7.28–7.49 (m, 5 H, 1 Ph). MALDI-MS (positive Mode, Matrix DHB, THF): 539.3 [M + K]$^+$. $C_{27}H_{32}O_7S$ (500.6): calcd. C 64.78, H 6.44; found C 64.54, H 6.81.

3β-*O*-(2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)cholesterol (10): TMSOTf solution (0.1 M *in* CH_2Cl_2, 130 μL, 0.05 equiv.) was added under vigorous stirring to a solution of the trichloroacetimidate **5** (160 mg, 0.294 mmol) and cholesterol (100 mg, 0.258 mmol) in dry CH_2Cl_2 (7 mL). After 15 min the reaction was treated with NEt_3 and concentrated. Repeated flash-chromatography of the residue (SiO_2, 3×21, PE/EtOAc, 5:1, then SiO_2, 3×12, PE/EtOAc, 10:1) yielded the saponin **10** (80 mg, 0.104 mmol, 41%). R_f(product) = 0.80 (petroleum ether/ethyl acetate, 3:1). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 0.65 (s, 3 H, 18′-H), 0.84 (d, $^3J_{26'/27',25'}$ = 6.5 Hz, 6 H, 26′-, 27′-H), 0.89 (d, $^3J_{21',20'}$ = 6.2 Hz, 3 H, 21′-H), 0.99 (s, 3 H, 19′-H), 1.05–1.74 (m, 21 H), 1.82–2.02 (m, 8 H, 2′-, 7′-, 8′-H, CH_3CO), 2.12–2.24 (m, 2 H, 4′-H), 3.39–3.49 (m, 2 H, 5-, 3′-H), 3.66–3.84 (m, 3 H, 3-, 4-H, 6-H_a), 4.32 (dd, $^2J_{6\text{-}Hb,6\text{-}Ha}$ = 10.3, $^3J_{6\text{-}Hb,5}$ = 5.1 Hz, 1 H, 6-H_b), 4.52 (d, $^3J_{1,2}$ = 8.4 Hz, 1 H, 1-H), 4.65–4.85 (2d, ^2J = 12.1 Hz, 2 H, CH_2Ph), 5.00 (dd, $^3J_{1,2}$ = $^3J_{2,3}$ = 8.4 Hz, 1 H, 2-H), 5.34 (s, 1 H, 6′-H), 5.56 (s, 1 H, PhCH), 7.24–7.48 (m, 10 H, 2 Ph). FAB-MS (positive Mode, Matrix NBA + NaI, THF): 791 [M + Na]$^+$. $C_{49}H_{68}O_7$·0.25H_2O (773.5): calcd. C 76.09, H 8.92; found C 76.00, H 9.67.

3′β-*O*-(3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-cholesterol (11). a) From 7: The glucal **7** (30 mg, 0.093 mmol) was dissolved in dry dichloromethane (2 mL) and cooled in an ice bath. A DMDO solution (1 mL, 0.1 M) was added dropwise to the stirred reaction mixture. The cooling bath was removed and stirring continued for 1.5 h until all starting material was consumed. All volatiles were evaporated under reduced pressure at room temp. The residue was redissolved together with cholesterol (60 mg, 0.150 mmol) in dry THF (2 mL) and the solution was cooled to –70 °C. Zinc chloride solution (250 μL, 0.5 M in THF, 0.125 mmol) was dropped slowly to the reaction mixture under argon. The reaction was warmed to room temp. overnight. Then the mixture was poured into saturated $NaHCO_3$ solution, extracted with diethyl ether, separated and concentrated. Flash chromatography (SiO_2 13×2, PE/EtOAc, 5:1) of the crude product afforded the saponin **11** (9 mg, 0.012 mmol, 13%). R_f(product) = 0.698 (petroleum ether/ethyl acetate, 2:1). R_f(acceptor) = 0.328 (petroleum ether/ethyl acetate, 2:1).

b) From 10: A solution of the acetylated saponin **10** (50 mg, 0.065 mmol) in dichloromethane/methanol (1:1, 3.0 mL) was treated with sodium methoxide (10 mg, 0.179 mmol). After complete deprotection the solution was neutralized with IR-120 (H^+), filtered and the solvents evaporated. Filtration through a short silica gel column (PE/EtOAc, 3:1) gave the deacetylated compound **11** (45 mg, 0.062 mmol, 95%). R_f(product) = 0.520 (petroleum ether/ethyl acetate, 3:1). R_f(starting material) = 0.620 (petroleum ether/ethyl acetate, 3:1).

c) From 12: The levulinoylated saponin **12** (10 mg, 12 μmol) was dissolved in CH_2Cl_2 (800 μL) and hydrazinium acetate solution (200 μL, 11% solution in CH_3OH, 24 μmol) was added. The reaction was stirred overnight, quenched with a few drops of acetone and concentrated. The crude product was separated by flash chromatography (SiO_2, 1×15, PE/EtOAc, 5:1) to yield the 2-OH free saponin **11** (7 mg, 9.6 μmol, 80%). R_f(product) = 0.52 (petro-

leum ether/ethyl acetate, 3:1). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 0.65 (s, 3 H, 18′-H), 0.84 (d, $^3J_{26'/27',25'}$ = 6.5 Hz, 6 H, 26′-, 27′-H), 0.89 (d, $^3J_{21',20'}$ = 6.2 Hz, 3 H, 21′-H), 0.99 (s, 3 H, 19′-H), 1.05–1.74 (m, 21 H), 1.82–2.02 (m, 5 H, 2′-, 7′-, 8′-H), 2.20–2.38 (m, 3 H, OH, 4′-H), 3.40–3.49 (m, 1 H, 5-H), 3.53–3.82 (m, 5 H, 2-, 3-, 4-H, 6-H_a, 3′-H), 4.30 (dd, $^2J_{6\text{-Hb},6\text{-Ha}}$ = 10.3, $^3J_{6\text{-Hb},5}$ = 4.8 Hz, 1 H, 6-H_b), 4.48 (d, $^3J_{1,2}$ = 7.5 Hz, 1 H, 1-H), 4.77–4.96 (2d, ^2J = 11.8 Hz, 2 H, CH_2Ph), 5.35 (d, $^3J_{6',7'\text{-Ha}}$ = 4.0 Hz, 1 H, 6′-H), 5.54 (s, 1 H, PhCH), 7.24–7.48 (m, 10 H, 2 Ph). $C_{47}H_{66}O_6$·0.5H_2O (736.0): calcd. C 76.69, H 9.17; found C 76.71, H 8.98.

3β-*O*-(3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-levulinoyl-β-D-glucopyranosyl)cholesterol (12): Cholesterol (60 mg, 0.160 mmol) and the thio donor **9** (90 mg, 0.180 mmol) were dried thoroughly under high vacuum. Freshly activated 4-Å molecular sieves (900 mg, powder) were added under argon and the mixture was suspended in dry CH_2Cl_2 (6.0 mL). DMTST (90 mg, 0.360 mmol, 2 equiv.) was added to the intensively stirred suspension. After disappearance of the acceptor (TLC: PE/EtOAc, 3:1) the reaction was quenched with NEt_3, the molecular sieves were filtered off, washed and the filtrate was concentrated. The residue was purified by flash chromatography (SiO_2, 2×16, petroleum ether/ethyl acetate, 5:1 → 4:1) to give the saponin **12** (90 mg, 0.109 mmol, 68%). R_f(product) = 0.48 (petroleum ether/ethyl acetate, 3:1). R_f(acceptor) = 0.33 (petroleum ether/ethyl acetate, 3:1). R_f(donor) = 0.24 (petroleum ether/ethyl acetate, 3:1). $[\alpha]_D$ = –1.3 (c = 0.03 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.65 (s, 3 H, 18′-H), 0.82 (d, $^3J_{26'/27',25'}$ = 6.5 Hz, 6 H, 26′-, 27′-H), 0.88 (d, $^3J_{21',20'}$ = 6.5 Hz, 3 H, 21′-H), 0.99 (s, 3 H, 19′-H), 1.04–1.74 (m, 21 H), 1.78–1.95 (m, 5 H, 2′-, 7′-, 8′-H), 2.10–2.32 (m, 5 H, 4′-H, H_3CCOCH$_2$CH$_2$CO), 2.45 (t, ^3J = 6.7 Hz, 2 H, H$_3$CCOCH$_2$CH_2CO), 2.64 (t, ^3J = 6.7 Hz, 2 H, H$_3$CCOCH_2CH$_2$CO), 3.33–3.40 (m, 2 H, 5-, 3′-H), 3.65 (dd, $^3J_{3,4}$ = $^3J_{3,2}$ = 9.1 Hz, 1 H, 3-H), 3.69 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 9.1 Hz, 1 H, 4-H), 3.74 (dd, $^2J_{6\text{-Ha},6\text{-Hb}}$ = $^3J_{6\text{-Ha},5}$ = 10.3 Hz, 1 H, 6-H_a), 4.26 (dd, $^2J_{6\text{-Hb},6\text{-Ha}}$ = 10.3, $^3J_{6\text{-Hb},5}$ = 4.9 Hz, 1 H, 6-H_b), 4.47 (d, $^3J_{1,2}$ = 9.1 Hz, 1 H, 1-H), 4.61–4.80 (2d, ^3J = 11.9 Hz, 2 H, CH_2Ph), 4.91 (dd, $^3J_{2,1}$ = $^3J_{2,3}$ = 9.1 Hz, 1 H, 2-H), 5.29 (d, $^3J_{6',7'}$ = 4.5 Hz, 1 H, 6′-H), 5.50 (s, 1 H, PhCH), 7.18–7.42 (m, 5 H, 1 Ph). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 11.8 (18′-CH_3), 18.7 (21′-CH_3), 19.3 (19′-CH_3), 21.0 (11′-C), 22.5 (26′-CH_3), 22.8 (27′-CH_3), 23.8 (23′-C), 24.2 (15′-C), 27.8 (OCOCH$_2$CH$_2$COCH_3), 28.0 (25′-C), 28.2 (12′-C), 29.6 (2′-C), 29.8/30.0 (OCOCH_2CH_2COCH$_3$), 31.8 (7′-, 8′-C), 35.7 (20′-C), 36.1 (22′-C), 37.2 (10′-C), 37.7 (1′-C), 38.8 (24′-C), 39.5 (16′-C), 39.7 (13′-C), 42.3 (4′-C), 50.1 (9′-C), 56.1 (17′-C), 56.7 (14′-C), 66.3 (5-C), 68.8 (6-C), 73.4 (2-C), 74.3 (PhCH_2), 78.4 (3-C), 79.8 (3′-C), 81.4 (4-C), 100.3 (1-C), 101.2 (PhCH), 122.0 (6′-C), 125.9–128.9 (10 Ph-C), 137.2/138.2 (2 Ph-C), 140.4 (5′-C), 171.2 (OCOCH$_2$CH$_2$COCH$_3$), 206.1 (OCOCH$_2$CH$_2$-COCH$_3$). $C_{52}H_{72}O_8$ (825.1): calcd. C 75.69, H 8.79; found C 75.65, H 9.03.

3β-*O*-[(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl]cholesterol (14): TMSOTf solution (0.02 M in CH_2Cl_2, 100 μL, 0.05 equiv.) was added to a solution of the acceptor **11** (30 mg, 0.041 mmol) in dry CH_2Cl_2 (1 mL). A solution of the trichloroacetimidate **13**[35] (40 mg in 1 mL dry CH_2Cl_2, 0.082 mmol) was dropped very slowly to the vigorously stirred reaction mixture. The glycosylation progress was followed intensively by TLC. After completion, the reaction was treated with NEt_3 and concentrated. Flash-chromatography (SiO_2, 2×20, PE/EtOAc, 3:1) of the residue yielded the disaccharide saponin **14** (30 mg, 0.028 mmol, 69%). R_f(product) = 0.56 (petroleum ether/ethyl acetate, 2:1). R_f(acceptor) = 0.76 (petroleum ether/ethyl acetate, 2:1). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 0.65 (s, 3 H, 18′-H), 0.84 (d, $^3J_{26'/27',25'}$ = 6.5 Hz, 6 H, 26′-, 27′-H), 0.89 (d, $^3J_{21',20'}$ = 6.2 Hz, 3 H, 21′-H), 0.99 (s, 3 H, 19′-H), 1.05–1.74 (m, 21 H), 1.82–2.02 (m, 14 H, 2′-, 7′-, 8′-H, 3 CH_3CO), 2.13 (s, 3 H, 1 CH_3CO), 2.30–2.34 (m, 2 H, 4′-H), 3.37 (m, 1 H, 5a-H), 3.53–3.78 (m, 5 H, 2a-, 3a-, 4a-H, 6a-H_a, 3′-H), 3.88 (ddd, $^3J_{5,4}$ = 0, $^3J_{5,6\text{-Ha}}$ = $^3J_{5,6\text{-Hb}}$ = 4.1 Hz, 1 H, 5b-H), 4.05–4.21 (m, 2 H, 6b-H_a, 6b-H_b), 4.30 (dd, $^2J_{6\text{-Hb},6\text{-Ha}}$ = 10.3, $^3J_{6\text{-Hb},5}$ = 4.8 Hz, 1 H, 6a-H_b), 4.57 (d, $^3J_{1,2}$ = 6.1 Hz, 1 H, 1a-H), 4.66–4.83 (2d, ^2J = 10.9 Hz, 2 H, CH_2Ph), 4.94–5.00 (m, 2 H, 1b-,3b-H), 5.18–5.25 (dd, $^3J_{2,1}$ = $^3J_{2,3}$ = 8.2 Hz, 1 H, 2b-H), 5.34 (m, 2 H, 4b-H, 6′-H), 5.53 (s, 1 H, PhCH), 7.24–7.42 (m, 10 H, 2 Ph). $C_{61}H_{84}O_{15}$·0.5H_2O (1066.3): calcd. C 68.70, H 8.05; found C 68.77, H 8.53.

3β-*O*-[(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)-4,6-*O*-benzylidene-β-D-glucopyranosyl]cholesterol (15). a) From 14: The benzylated compound **14** (10 mg, 9.5 μmol) was dissolved in deoxygenated dichloromethane/ethanol (1:1, 1 mL). The resulting solution was added to prehydrogenated Pd/C catalyst (2 mg) suspended in deoxygenated dichloromethane/methanol (1:1, 1 mL). The reaction mixture was vigorously stirred under hydrogen. Thorough TLC control (PE/EtOAc, 2:1) indicated only modest and incomplete debenzylation. The mixture was concentrated and the residue transferred to flash chromatography (SiO_2, PE/EtOAc, 4:1 → 3:1) to give the debenzylated saponin **15** (2 mg, 2.07 mmol, 22%).

b) From 24: The debenzylated compound **24** (290 mg, 0.330 mmol) was dissolved in acetonitrile (7 mL). Benzaldehyde dimethyl acetal (60 μL, 0.400 mmol) and camphersulfonic acid (10 mg, 0.04 mmol) were added. After 6 h NEt_3 was used to quench and the reaction mixture was concentrated. Flash chromatography (SiO_2, 3×12, PE/EtOAc, 5:1 → 3:1 → 2:1 → 1:1) gave the benzylidenated compound **15** (230 mg, 0.238 mmol, 72%). R_f(product) = 0.51 (petroleum ether/ethyl acetate, 1:1). $[\alpha]_D$ = –4.9 (c = 0.1 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.65 (s, 3 H, 18′-H), 0.82 (d, $^3J_{26'/27',25'}$ = 6.5 Hz, 6 H, 26′-, 27′-H), 0.88 (d, $^3J_{21',20'}$ = 6.5 Hz, 3 H, 21′-H), 0.99 (s, 3 H, 19′-H), 1.04–1.74 (m, 21 H), 1.83–2.14 (m, 17 H, 2′-, 7′-, 8′-, 4 H_3CCO), 2.28–2.32 (m, 2 H, 4′-H), 2.68 (d, $^3J_{OH,3}$ = 2.8 Hz, 1 H, OH), 3.38 (m, 1 H, 5a-H), 3.49–3.58 (m, 3 H, 2a-, 4a-, 3′-H), 3.74 (dd, $^2J_{6\text{-Ha},6\text{-Hb}}$ = $^3J_{6\text{-Ha},5}$ = 10.3 Hz, 1 H, 6a-H_a), 3.83 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 9.0 Hz, 1 H, 3a-H), 3.98 (ddd, $^3J_{5,4}$ = 0, $^3J_{5,6\text{-Ha}}$ = $^3J_{5,6\text{-Hb}}$ = 6.7 Hz, 1 H, 5b-H), 4.09 (dd, $^2J_{6\text{-Ha},6\text{-Hb}}$ = 11.1, $^3J_{6\text{-Ha},5}$ = 6.7 Hz, 1 H, 6b-H_a), 4.19 (dd, $^2J_{6\text{-Hb},6\text{-Ha}}$ = 11.1, $^3J_{6\text{-Hb},5}$ = 6.7 Hz, 1 H, 6b-H_b), 4.30 (dd, $^2J_{6\text{-Hb},6\text{-Ha}}$ = 10.5, $^3J_{6\text{-Hb},5}$ = 5.0 Hz, 1 H, 6a-Hb), 4.61 (d, $^3J_{1,2}$ = 7.5 Hz, 1 H, 1a-H), 4.92 (d, $^3J_{1,2}$ = 7.9 Hz, 1 H, 1b-H), 5.04 (dd, $^3J_{3,2}$ = 10.6, $^3J_{3,4}$ = 3.4 Hz, 1 H, 3b-H), 5.23 (dd, $^3J_{2,3}$ = 10.6, $^3J_{2,1}$ = 7.9 Hz, 1 H, 2b-H), 5.33 (d, $^3J_{6',7'}$ = 4.7 Hz, 1 H, 6′-H), 5.39 (dd, $^3J_{4,3}$ = 3.4, $^3J_{4,5}$ < 1 Hz, 1 H, 4b-H), 5.51 (s, 1 H, PhCH), 7.32–7.48 (m, 5 H, 1 Ph). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 11.8 (18′-CH_3), 18.7 (21′-CH_3), 19.3 (19′-CH_3), 20.6 (4 OCOCH_3), 21.0 (11′-C), 22.5 (26′-CH_3), 22.8 (27′-CH_3), 23.8 (23′-C), 24.2 (15′-C), 28.0 (25′-C), 28.2 (12′-C), 29.8 (2′-C), 31.8 (7′-, 8′-C), 35.7 (20′-C), 36.1 (22′-C), 37.0 (10′-C), 37.7 (1′-C), 38.9 (24′-C), 39.5 (16′-C), 39.7 (13′-C), 42.3 (4′-C), 50.0 (9′-C), 56.1 (17′-C), 56.7 (14′-C), 60.7 (6b-C), 65.8 (5a-C), 66.6 (4b-C), 68.6 (6a-C), 69.9 (2b-C), 70.7 (3b-, 5b-C), 72.5 (3a-C), 79.8 (3′-, 4a-C), 83.2 (2a-C), 100.9 (1a-C), 101.6 (1b-C), 101.8 (PhCH), 122.2 (6′-C), 126.2 (2 Ph-C), 128.3 (2 Ph-C), 129.2 (1 Ph-C), 136.8 (1 Ph-C), 140.1 (5′-C), 170.2–170.6 (4 OCOCH$_3$). $C_{54}H_{78}O_{15}$·0.5H_2O (976.2): calcd. C 66.44, H 8.15; found C 66.41, H 8.00.

3β-*O*-{(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→3)]-4,6-*O*-benzylidene-β-D-glucopyranosyl}cholesterol (17). a) Inverse Addition: A TMSOTf solution (20 μL, 0.02 M in CH_2Cl_2, 0.05 equiv.) was added to a solu-

tion of the acceptor 15 (7 mg, 7.7 μmol) in dry CH_2Cl_2 (300 μL). Trichloroacetimidate 16[36] (10 mg, 20 μmol) dissolved in dry CH_2Cl_2 (50 μL) was added portionwise at room temp. The reaction was quenched with NEt_3, concentrated and separated by flash chromatography (SiO_2, 1×17, PE/EtOAc, 2:1 → 1:1) to give the trisaccharide saponin 17 (6 mg, 4.9 μmol, 64%). R_f(product) = 0.48 (petroleum ether/ethyl acetate, 1:1).

b) Normal Addition: A TMSOTf solution (0.10 M in CH_2Cl_2, 30 μL, 0.03 equiv.) was added to a solution of acceptor **15** (100 mg, 0.103 mmol) and trichloroacetimidate **16** (60 mg, 0.134 mmol) in dry CH_2Cl_2 (3 mL). After 20–30 min the glycosylation was quenched with NEt_3, the solvent was evaporated and the residue applied to repeated flash chromatography (SiO_2, 3×11, PE/EtOAc, 2:1 → 1:1) to yield the trisaccharide saponin **17** (90 mg, 0.074 mmol, 71%). R_f(product) = 0.45 (petroleum ether/ethyl acetate, 2:1, two runs). R_f(acceptor) = 0.55 (petroleum ether/ethyl acetate, 2:1, two runs). $[\alpha]_D$ = –2.4 (c = 0.04, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.67 (s, 3 H, 18′-H), 0.85 (2d, $^3J_{26'/27',25'}$ = 2.5 Hz, 6 H, 26′-, 27′-H), 0.90 (d, $^3J_{21',20'}$ = 6.0 Hz, 3 H, 21′-H), 1.00 (s, 3 H, 19′-H), 1.07–1.62 (m, 21 H), 1.79–1.80 (m, 3 H, 7′-, 8′-H), 1.96–2.09 (m, 20 H, 2′-H, 6 H_3CCO), 2.13 (s, 3 H, 1 H_3CCO), 2.24–2.40 (m, 2 H, 4′-H), 3.20 (dd, $^2J_{5\text{-Ha},5\text{-Hb}}$ = 12.3, $^3J_{5\text{-Ha},4}$ = 6.0 Hz, 1 H, 5c-H_a), 3.39 (m, 1 H, 5a-H), 3.51 (m, 1 H, 3′-H), 3.61 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 9.4 Hz, 1 H, 4a-H), 3.74 (dd, $^2J_{6\text{-Ha},6\text{-Hb}}$ = $^3J_{6\text{-Ha},5}$ = 10.3 Hz, 1 H, 6a-H_a), 3.77 (dd, $^3J_{2,3}$ = $^3J_{2,1}$ = 7.8 Hz, 1 H, 2a-H), 3.96 (m, 1 H, 5b-H), 3.99 (dd, $^3J_{3,4}$ = $^3J_{3,2}$ = 8.9 Hz, 1 H, 3a-H), 4.15 (m, 2 H, 6b-H_a, 6b-H_b), 4.20 (dd, $^2J_{5\text{-Hb},5\text{-Ha}}$ = 12.3, $^3J_{5\text{-Hb},4}$ = 3.8 Hz, 1 H, 5c-H_b), 4.31 (dd, $^2J_{6\text{-Hb},6\text{-Ha}}$ = 10.3, $^3J_{6\text{-Hb},5}$ = 4.9 Hz, 1 H, 6a-H_b), 4.51 (d, $^3J_{1,2}$ = 7.4 Hz, 1 H, 1 H, 1a-H), 4.80 (m, 1 H, 4c-H), 4.91 (d, $^3J_{2,1}$ = 4.4, $^3J_{2,3}$ = 5.9 Hz, 1 H, 2c-H), 4.92 (d, $^3J_{1,2}$ = 7.6 Hz, 1 H, 1b-H), 4.99 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 6.2 Hz, 1 H, 3c-H), 5.00 (d, $^3J_{1,2}$ = 4.0 Hz, 1 H, 1c-H), 5.11 (dd, $^3J_{2,3}$ = $^3J_{2,1}$ = 7.7 Hz, 1 H, 2b-H), 5.14 (dd, $^3J_{3,2}$ = 10.4, $^3J_{3,4}$ = 3.2 Hz, 1 H, 3b-H), 5.35 (ddd, $^3J_{4,3}$ = 3.2, $^3J_{4,5}$ < 1 Hz, 1 H, 4b-H), 5.39 (dd, $^3J_{6',7'}$ = 3.0 Hz, 1 H, 6′-H), 5.49 (s, 1 H, PhCH), 7.35 (m, 3 H, Ph), 7.43 (m, 2 H, Ph). ^{13}C NMR (151 MHz, $CDCl_3$, selected data, ppm): δ = 60.4 (5c-C), 61.1 (6b-C), 65.9 (5a-C), 67.4 (4b-C), 67.5 (4c-C), 69.0 (6a-C), 69.4 (3c-C), 69.7 (2c-C), 70.3 (2b-C), 70.6 (5b-C), 70.7 (3b-C), 77.4 (3a-C), 79.3 (4a-C), 79.8 (2a-C), 80.4 (3′-C), 97.9 (1c-C), 99.5 (1b-C), 101.0 (1a-C), 101.7 (Ph*C*H), 121.9 (6′-C), 126.0 (2 Ph-C), 128.2 (2 Ph-C), 129.2 (1 Ph-C), 140.5 (5′-C), 169.2–170.2 (7 O*C*OCH$_3$). $C_{65}H_{92}O_{22}$·H_2O (1243.4): calcd. C 63.24, H 7.59; found C 63.29, H 7.51.

3β-*O*-{(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→3)]-β-D-glucopyranosyl}cholesterol (18). a) From 17: The benzylidenated compound **17** (50 mg, 0.041 mmol) was dissolved in CH_2Cl_2 (0.5 mL) an treated with ethanethiol (20 μL). This solution was slightly acidified with *p*-toluenesulfonic acid. After 2 h vigorous stirring the solution was quenched with NEt_3 and concentrated. Purification by column chromatography (SiO_2, 2×4, PE/EtOAc, 1:1) gave the debenzylidenated saponin 18 (40 mg, 0.035 mmol, 86%) as white solid.

b) From 33: The compound **33** (60 mg, 0.047 mmol) was dissolved in dry THF (2 mL) in a teflon flask. Pyridine hydrogen fluoride (60 μL, 70% HF) was added dropwise to the well stirred solution. Stirring was continued for 1 h. The reaction was diluted with dichloromethane and washed with saturated $NaHCO_3$ solution. The dichloromethane layer was evaporated and the crude product passed through a short silica gel column (PE/EtOAc, 1:2) to give the desilylated saponin **18** (50 mg, 0.044 mmol, 94%). R_f(product) = 0.16 (petroleum ether/ethyl acetate, 2:1). $[\alpha]_D$ = –4.4 (c = 0.1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.67 (s, 3 H, 18′-CH_3), 0.85 (2d, $^3J_{26'/27',25'}$ = 2.4 Hz, 6 H, 26′-, 27′-CH_3), 0.90 (d, $^3J_{21',20'}$ = 6.4 Hz, 3 H, 21′-CH_3), 1.00 (s, 3 H, 19′-CH_3), 1.07–1.62 (m, 21 H), 1.81–1.87 (m, 3 H, 7′-, 8′-H), 1.98 (s, 3 H, 1 CH_3CO), 1.99–2.05 (m, 11 H, 2′-H, 3 CH_3CO), 2.08 (3s, 6 H, 2 CH_3CO), 2.13 (s, 3 H, 1 CH_3CO), 2.31–2.33 (m, 2 H, 4′-H), 3.30 (m, 1 H, 5a-H), 3.41 (dd, $^2J_{5\text{-Ha},5\text{-Hb}}$ = 11.7, $^3J_{5\text{-Ha},4}$ = 2.7 Hz, 1 H, 5c-H_a), 3.44 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 9.2 Hz, 1 H, 4a-H), 3.52 (m, 1 H, 3′-H), 3.61 (dd, $^3J_{2,3}$ = $^3J_{2,1}$ = 7.9 Hz, 1 H, 2a-H), 3.73 (m, 2 H, 3a, 6a-H_a), 3.90 (m, 2 H, 5b-, 6a-H_b), 4.15 (m, 2 H, 6b-H_a, 6b-H_b), 4.18 (dd, $^2J_{5\text{-Hb},5\text{-Ha}}$ = 11.9, $^3J_{5\text{-Hb},4}$ = 5.1 Hz, 1 H, 5c-H_b), 4.55 (d, $^3J_{1,2}$ = 7.6 Hz, 1 H, 1a-H), 4.81 (d, $^3J_{1,2}$ = 6.7 Hz, 1 H, 1c-H), 4.84 (d, $^3J_{1,2}$ = 7.8 Hz, 1 H, 1b-H), 4.95–4.99 (m, 2 H, 2c-, 4c-H), 5.01 (dd, $^3J_{3,2}$ = 10.4, $^3J_{3,4}$ = 3.2 Hz, 1 H, 3b-H), 5.14 (dd, $^3J_{2,1}$ = 7.6, $^3J_{2,3}$ = 10.3 Hz, 1 H, 2b-H), 5.19 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 8.6 Hz, 1 H, 3c-H), 5.36 (m, 2 H, 4b-, 6′-H). ^{13}C NMR (151 MHz, $CDCl_3$, selected data, ppm): δ = 11.8 (18′-C), 18.7 (21′-C), 19.3 (19′-C), 22.5 (26′-C), 22.8 (27′-C), 61.1 (6b-C), 62.1 (5c-C), 62.9 (6a-C), 66.7 (4b-C), 68.5 (4c-C), 69.7 (4a-C), 69.8 (2b-C), 70.6 (5b-C), 70.8 (3b-C), 71.1 (3c-, 2c-C), 74.9 (5a-C), 78.4 (2a-C), 79.9 (3′-C), 84.3 (3a-C), 98.8 (1b-C), 99.6 (1a-C), 100.3 (1c-C), 122.2 (6′-C), 140.2 (5′-C), 169.3–170.2 (7 O*C*OCH$_3$). $C_{58}H_{88}O_{22}$·0.25H_2O (1141.8): calcd. C 61.01, H 7.81; found C 60.97, H 8.15.

3β-*O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)cholesterol (21): A vigorously stirred solution of cholesterol (540 mg, 1.40 mmol) and trichloroacetimidate **19**[37,38] (980 mg, 1.54 mmol) in dry CH_2Cl_2 (35 mL) was activated by TMSOTf solution (0.1 M in CH_2Cl_2, 280 μL, 0.02 equiv.). After 15 min the reaction was complete. The reaction was quenched with NEt_3 and concentrated. Flash chromatography (SiO_2, 50 g, PE/EtOAc, 8:1) of the residue yielded the acetylated saponin **21** (1.06 g, 1.23 mmol, 88%). R_f(product) = 0.62 (petroleum ether/ethyl acetate, 4:1) which was immediately used in the next step. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 0.70 (s, 3 H, 18′-H), 0.88 (d, $^3J_{26'/27',25'}$ = 6.6 Hz, 6 H, 26′-, 27′-H), 0.94 (d, $^3J_{21',20'}$ = 6.4 Hz, 3 H, 21′-H), 1.01 (s, 3 H, 19′-H), 1.02–1.70 (m, 21 H), 1.86 (m, 2 H, 7′-H), 2.00 (m, 6 H, 2′-, 8′-H, 1 CH_3CO), 2.20–2.25 (m, 2 H, 4′-H), 3.48–3.80 (m, 6 H, 3-, 4-, 5-, 3′-H, 6-H_a, 6-H_b), 4.45 (d, $^3J_{1,2}$ = 8.0 Hz, 1 H, 1a-H), 4.55–4.84 (m, 6 H, 3 CH_2Ph), 4.99 (dd, $^3J_{2,3}$ = 9.4, $^3J_{2,1}$ = 8.0 Hz, 1 H, 2a-H), 5.36 (d, $^3J_{6',7'}$ = 4.7 Hz, 1 H, 6′-H), 7.20–7.36 (m, 15 H, 3 Ph).

3β-*O*-(3,4,6-Tri-*O*-benzyl-β-D-glucopyranosyl)cholesterol (22). a) From 21: Compound **21** (200 mg, 0.232 mmol) was deacetylated by dissolving in methanol/dioxane (1:2, 7.5 mL) and treating with 7 drops of 1 M NaOH solution. After stirring overnight the deacetylation was complete (TLC toluene/acetone, 10:1). The solution was neutralized with IR-120 (H^+), filtered and the solvents evaporated. Further purification of the product **22** was not necessary.

b) From 20: A freshly prepared solution of DMDO (18 mL, 0.1 M in acetone, 1.8 mmol) was added to an ice-cold solution of the glucal **20**[39] (600 mg, 1.44 mmol) in dry dichloromethane (30 mL). The cooling bath was removed and the reaction was stirred at room temp. for 1 h to complete the epoxidation reaction. The volatiles were evaporated under reduced pressure at 25 °C; the epoxide was thoroughly dried under high vacuum, mixed with cholesterol **26** and dissolved in dry THF (30 mL). The solution was cooled to –70 °C and zinc chloride solution (1.8 mL, 1 M in THF, 1.8 mmol) was added under argon atmosphere. The cooling bath was removed, the temperature raised to 25 °C overnight and the reaction stirred for further 36 h. The mixture was quenched by NEt_3, concentrated and chromatographed (SiO_2, 4×13, PE/EtOAc, 7:1 → 5:1) to yield the saponin **22** (500 mg, 0.611 mmol, 42%). Remark: Replacement of zinc chloride in THF by zinc chloride in Et_2O led

in some cases to higher yields. R_f(product) = 0.57 (petroleum ether/ethyl acetate, 4:1). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.69 (s, 3 H, 18′-H), 0.87 (d, $^3J_{26'/27',25'}$ = 6.7 Hz, 6 H, 26′-, 27′-H), 0.92 (d, $^3J_{21',20'}$ = 6.6 Hz, 3 H, 21′-H), 1.01 (s, 3 H, 19′-H), 1.02–1.70 (m, 21 H), 1.86 (m, 2 H, 7′-H), 2.00 (m, 3 H, 2′-, 8′-H), 2.32–2.37 (m, 3 H, OH, 4′-H), 3.48–3.59 (m, 5 H, 2-, 3-, 4-, 5-, 3′-H), 3.67 (dd, $^2J_{6\text{-}Ha,6\text{-}Hb}$ = 9.6, $^3J_{6\text{-}Ha,5}$ = 5.4 Hz, 1 H, 6-Ha), 3.74 (dd, $^2J_{6\text{-}Hb,6\text{-}Ha}$ = 9.6, $^3J_{6\text{-}Hb,5} < 1$ Hz, 1 H, 6-Hb), 4.36 (d, $^3J_{1,2}$ = 7.8 Hz, 1 H, 1a-H), 4.54–4.96 (m, 6 H, 3 CH_2Ph), 5.36 (d, $^3J_{6',7'}$ = 1.8 Hz, 1 H, 6′-H), 7.18–7.39 (m, 15 H, 3 Ph). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 11.8 (18′-CH_3), 18.7 (21′-CH_3), 19.3 (19′-CH_3), 21.0 (11′-C), 22.5 (26′-CH_3), 22.8 (27′-CH_3), 23.8 (23′-C), 24.2 (15′-C), 28.0 (25′-C), 28.2 (12′-C), 29.8 (2′-C), 31.8 (7′-, 8′-C), 35.7 (20′-C), 36.1 (22′-C), 36.7 (10′-C), 37.2 (1′-C), 38.9 (24′-C), 39.5 (16′-C), 39.7 (13′-C), 42.3 (4′-C), 50.1 (9′-C), 56.1 (17′-C), 56.7 (14′-C), 69.1 (6-C), 73.5 (1 Ph*C*H_2), 74.7 (2-C), 75.1 (2 Ph*C*H_2, 5-C), 77.7 (3-C), 79.2 (3′-C), 84.6 (4-C), 101.2 (1-C), 122.0 (6′-C), 127.5–128.4 (15 Ph-C), 138.0/138.2/138.6 (3 Ph-C), 140.4 (5′-C). $C_{54}H_{74}O_6$ (819.1): calcd. C 79.18, H 9.10; found C 78.81, H 8.73.

3β-*O*-[(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl]cholesterol (23): TMSOTf solution (0.1 M in CH_2Cl_2, 150 μL, 0.03 equiv.) was added to a vigorously stirred solution of the saponin acceptor **22** (420 mg, 0.513 mmol) in dry CH_2Cl_2 (15 mL). The trichloracetimidate **1**3 (380 mg, 0.772 mmol) dissolved in dry CH_2Cl_2 (5 mL) was added dropwise to the well stirred solution. After 20 min the reaction was treated with NEt_3 and concentrated. Flash chromatography (SiO_2, 4×10, PE/EtOAc, 5:1 → 4:1 → 3:1) of the residue yielded the disaccharide saponin **23** (450 mg, 0.392 mmol, 76%). R_f(product) = 0.48 (petroleum ether/ethyl acetate, 3:1). R_f(acceptor) = 0.66 (petroleum ether/ethyl acetate, 3:1). $[\alpha]_D$ = –4.5 (c = 0.1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.69 (s, 3 H, 18′-H), 0.87 (d, $^3J_{26'/27',25'}$ = 6.7 Hz, 6 H, 26′-, 27′-H), 0.92 (d, $^3J_{21',20'}$ = 6.6 Hz, 3 H, 21′-H), 1.01 (s, 3 H, 19′-H), 1.02–1.70 (m, 21 H), 1.86 (m, 5 H, 7′-H, 1 H_3CCO), 1.96–2.06 (m, 9 H, 2′-, 8′-H, 2 CH_3CO), 2.16 (s, 3 H, 1 CH_3CO), 2.34 (m, 2 H, 4′-H), 3.42 (m, 1 H, 5a-H), 3.56–3.70 (m, 6 H, 2a-, 3a-, 4a-, 6a-H_a, 6a-H_b, 3′-H), 3.94 (ddd, $^3J_{5,4}$ = 0, $^3J_{5,6\text{-}Ha}$ = $^3J_{5,6\text{-}Hb}$ = 6.8 Hz, 1 H, 5b-H), 4.11 (m, 1 H, 6b-H_a), 4.21 (dd, $^2J_{6\text{-}Hb,6\text{-}Ha}$ = 11.1, $^3J_{6\text{-}Hb,5}$ = 7.9 Hz, 1 H, 6b-H_b), 4.49–4.85 (m, 7 H, 3 CH_2Ph, 1a-H), 4.99 (dd, $^3J_{3,2}$ = 7.8, $^3J_{3,4}$ = 3.0 Hz, 1 H, 3b-H), 5.07 (d, $^3J_{1,2}$ = 8.1 Hz, 1 H, 1b-H), 5.22 (dd, $^3J_{2,3}$ = 7.8, $^3J_{2,1}$ = 8.1 Hz, 1 H, 2b-H), 5.34 (s, 1 H, 6′-H), 5.38 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 3 Hz, 1 H, 4b-H), 7.09–7.35 (m, 15 H, 3Ph). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 11.8 (18′-CH_3), 18.7 (21′-CH_3), 19.3 (19′-CH_3), 20.6 (4 OCO*C*H_3), 21.0 (11′-C), 22.5 (26′-CH_3), 22.8 (27′-CH_3), 23.8 (23′-C), 24.2 (15′-C), 28.0 (25′-C), 28.2 (12′-C), 29.8 (2′-C), 31.8 (7′-, 8′-C), 35.7 (20′-C), 36.1 (22′-C), 37.0 (10′-C), 37.7 (1′-C), 39.0 (24′-C), 39.5 (16′-C), 39.7 (13′-C), 42.3 (4′-C), 50.0 (9′-C), 56.1 (17′-C), 56.7 (14′-C), 61.0 (6b-C), 66.8 (4b-C), 68.8 (6a-C), 70.1 (2b-C), 70.7 (5b-C), 71.3 (3b-C), 73.5 (1 Ph*C*H_2), 74.6 (5a-C), 75.0/76.2 (2 Ph*C*H_2), 78.2 (4a-C), 79.7 (3′-C), 91.0 (2a-C), 84.5 (3a-C), 100.3 (1b-C), 100.8 (1a-C), 121.9 (6′-C), 127.5–128.3 (15 Ph-C), 137.8/138.0/138.4 (3 Ph-C), 140.4 (5′-C), 169.3–170.2 (4 O*C*OCH$_3$).

3β-*O*-[(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)-β-D-glucopyranosyl]cholesterol (24). a): The benzylated compound **23** (390 mg, 0.339 mmol) was dissolved in dry ethanol/dichloromethane (2:1, 9 mL) and the Pd/C catalyst (25 mg, 10% Pd) suspended in the solution. This mixture was stirred for 1–3 h under hydrogen atmosphere. After disappearance of the starting material, the catalyst was filtered off and all solvents were removed. The residue **24** (290 mg, qu) could be used without further purification but filtration was carried out by passing it through a short silica gel column (toluene/acetone, 1:1). Remark: In some cases it was necessary to activate the Pd/C catalyst by prehydrogenation before adding the starting material.

b) Alternative procedure [with Pearlman catalyst Pd(OH)$_2$]: Pd-(OH)$_2$/C (50 mg, 20% Pd) was suspended in deoxygenated ethanol (2 mL). The suspension was hydrogenated for 10 min. Then a solution of the starting material **23** (100 mg, 0.087 mmol) in dioxane (700 μL) was added. The mixture was stirred for 1–3 h under hydrogen atmosphere until the reaction was complete. The catalyst was filtered off and the solvents were removed. The residue **24** (70 mg, 0.080 mmol, 92%) was sufficiently pure for the next step. R_f(product) = 0.22 (toluene/acetone, 1:1). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.69 (s, 3 H, 18′-H), 0.87 (d, $^3J_{26'/27',25'}$ = 6.7 Hz, 6 H, 26′-, 27′-H), 0.92 (d, $^3J_{21',20'}$ = 6.6 Hz, 3 H, 21′-H), 1.01 (s, 3 H, 19′-H), 1.02–1.70 (m, 21 H), 1.86–2.15 (m, 17 H, 2′-, 7′-, 8′-H, 4 H_3CCO), 2.30 (m, 2 H, 4′-H), 3.33 (m, 2 H, 2a-, 5a-H), 3.52–3.57 (m, 3 H, 3a-, 4a-, 3′-H), 3.76 (dd, $^2J_{6\text{-}Ha,6\text{-}Hb}$ = 10.8, $^3J_{6\text{-}Ha,5}$ = 5.1 Hz, 1 H, 6a-H_a), 3.88 (dd, $^2J_{6\text{-}Hb,6\text{-}Ha}$ = 10.8, $^3J_{6\text{-}Hb,5}$ = 3.2 Hz, 1 H, 6a-H_b), 3.99 (ddd, $^3J_{5,4}$ = 0, $^3J_{5,6\text{-}Ha}$ = $^3J_{5,6\text{-}Hb}$ = 5.6 Hz, 1 H, 5b-H), 4.09 (dd, $^2J_{6\text{-}Ha,6\text{-}Hb}$ = 11.0, $^3J_{6\text{-}Ha,5}$ = 5.6 Hz, 1 H, 6b-H_a), 4.21 (dd, $^2J_{6\text{-}Hb,6\text{-}Ha}$ = 11.0, $^3J_{6\text{-}Hb,5}$ = 5.6 Hz, 1 H, 6b-Hb), 4.56 (d, $^3J_{1,2}$ = 7.6 Hz, 1 H, 1a-H), 4.92 (d, $^3J_{1,2}$ = 8.4 Hz, 1 H, 1b-H), 5.04 (dd, $^3J_{3,2}$ = 7.4, $^3J_{3,4}$ = 2.7 Hz, 1 H, 3b-H), 5.24 (dd, $^3J_{2,3}$ = 7.4, $^3J_{2,1}$ = 8.4 Hz, 1 H, 2b-H), 5.31 (d, $^3J_{6',7'}$ = 4.0 Hz, 1 H, 6′-H), 5.40 (dd, $^3J_{4,3}$ = 2.7, $^3J_{4,5} < 1$ Hz, 1 H, 4b-H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 11.8 (18′-CH_3), 18.7 (21′-CH_3), 19.3 (19′-CH_3), 20.6 (4 OCO*C*H_3), 21.0 (11′-C), 22.5 (26′-CH_3), 22.8 (27′-CH_3), 23.8 (23′-C), 24.2 (15′-C), 28.0 (25′-C), 28.2 (12′-C), 29.8 (2′-C), 31.8 (7′-, 8′-C), 35.7 (20′-C), 36.1 (22′-C), 37.0 (10′-C), 37.7 (1′-C), 38.9 (24′-C), 39.5 (16′-C), 39.7 (13′-C), 42.3 (4′-C), 50.0 (9′-C), 56.1 (17′-C), 56.7 (14′-C), 60.7 (6b-C), 62.5 (6a-C), 66.5 (4b-C), 70.1 (4a-, 2b-C), 70.5 (3b-C), 70.9 (5b-C), 74.8 (5a-C), 75.2 (3a-C), 78.7 (3′-C), 82.3 (2a-C), 100.5 (1a-C), 101.2 (1b-C), 122.3 (6′-C), 140.0 (5′-C), 170.1–171.1 (4 O*C*OCH$_3$).

Ethyl (2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl)-(1→3)-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (26): The thio compound **25**[42] (360 mg, 1.154 mmol) and freshly activated molecular sieves (300 mg, 3 Å AW) were suspended in dry dichloromethane (70 mL). The suspension was cooled to –75 °C and activated by TMSOTf (50 μL of a 0.1 M solution in CH_2Cl_2, 5 μmol, 0.005 equiv.). A cold solution of the donor **16** (420 mg, 1.0 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise to the cold reaction mixture (in this time the cooling bath temperature was allowed to reach –55 °C) and the solution became turbid due to precipitated trichloroacetimidate. Thorough TLC control indicated to stop the reaction at –55 °C with NEt_3. The molecular sieves were filtered off and the solvent was evaporated. The residue was separated by flash chromatography (SiO_2, 300 g, PE/EtOAc, 2:1 → 3:2 → 1:1 → 1:2) to give the disaccharide **26** (250 mg, 0.439 mmol, 86%) and reisolated acceptor (200 mg, 0.641 mmol). R_f(product) = 0.44 (petroleum ether/ethyl acetate, 1:1). $[\alpha]_D$ = –6.7 (c = 0.1, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 1.22–1.32 (m, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.01 (3s, 9 H, 3 H_3CCO), 2.68 (s, 1 H, OH), 2.73 (m ^3J = 7.4 Hz, 2 H,, 2 H, SCH_2CH_3), 3.21 (dd, $^2J_{5\text{-}Ha,5\text{-}Hb}$ = 12.4, $^3J_{5\text{-}Ha,4}$ = 7.7 Hz, 1 H, 5b-H_a), 3.40–3.85 (m, 5 H, 2a-, 3a-, 4a-, 5a-H, 6a-H_a), 4.12 (dd, $^2J_{5\text{-}Hb,5\text{-}Ha}$ = 12.4, $^3J_{5\text{-}Hb,4}$ = 4.8 Hz, 1 H, 5b-H_b), 4.32 (dd, $^2J_{6\text{-}Hb,6\text{-}Ha}$ = 10.5, $^3J_{6\text{-}Hb,5}$ = 4.9 Hz, 1 H, 6a-H_b), 4.42 (d, $^3J_{1,2}$ = 9.8 Hz, 1 H, 1a-H), 4.84 –4.95 (m, 1 H, 1b-, 2b-, 4b-H), 5.09 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 6.2 Hz, 1 H, 3b-H), 5.51 (s, 1 H, PhCH), 7.34 (m, 3 H, Ph), 7.43 (m, 2 H, Ph). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 15.2 (SCH_2CH_3), 20.6/20.7/20.8 (3 OCO*C*H_3), 24.6 (SCH_2CH_3), 61.6 (5b-C), 68.6 (4b, 6a-C), 70.6 (3b-C), 70.8

(5a-C), 71.0 (2b-C), 72.9 (2a-C), 79.3 (4a-C), 81.0 (3a-C), 86.5 (1a-C), 100.5 (1b-C), 101.4 (Ph*C*H), 125.9 (2 Ph-C), 128.2 (2 Ph-C), 129.0 (1 Ph-C), 137.0 (1 Ph-C), 169.8–170.0 (3 O*C*OCH$_3$). $C_{26}H_{34}O_{12}S$ (668.7): calcd. C 54.73, H 6.00; found C 54.51, H 5.89.

Ethyl (2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-*O*-levulinoyl-1-thio-β-D-glucopyranoside (27): The OH-free compound **26** (200 mg, 0.351 mmol) was dissolved in dry CH_2Cl_2 (10 mL). Levulinic acid anhydride (110 mg, 0.515 mmol) was added and the reaction was activated by the addition of triethylamine (70 μL, 0.50 mmol) and DMAP (30 mg, 0.246 mmol). The reaction was stirred for 5 h until the starting material **26** was nearly completely consumed (HPTLC: PE/EtOAc, 1:1). The reaction was quenched by NEt_3, diluted with CH_2Cl_2 and treated with saturated $NaHCO_3$ solution. Separation and evaporation of the organic layer gave a residue, which was purified by flash chromatography (SiO_2, PE/EtOAc, 3:1 → 2:1) to afford the levulinoylated compound **27** (220 mg, 0.329 mmol, 94%) as a white solid. R_f(product) = 0.59 (HPTLC, petroleum ether/ethyl acetate, 1:1). R_f(starting material) = 0.66 (HPTLC, petroleum ether/ethyl acetate, 1:1). $[\alpha]_D$ = –9.1 (*c* = 0.1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 1.23 (t, ^3J = 6.1 Hz, 3 H, SCH$_2$C*H*$_3$), 2.00 (3s, 9 H, 3 H$_3$CCO), 2.18 (s, 3 H, *H*$_3$CCOCH$_2$CH$_2$CO), 2.50–2.73 (m, 4 H, H$_3$CCOC*H*$_2$C*H*$_2$CO), 2.79 (q, ^3J = 6.1 Hz, 2 H, SC*H*$_2$CH$_3$), 3.30 (dd, $^2J_{5\text{-Ha},5\text{-Hb}}$ = 12.3, $^3J_{5\text{-Ha},4}$ = 6.8 Hz, 1 H, 5b-H$_a$), 3.49 (m, 1 H, 5a-H), 3.65 (dd, $^3J_{4,5}$ = $^3J_{4,3}$ = 9.4 Hz, 1 H, 4a-H), 3.75 (dd, $^2J_{6\text{-Ha},6\text{-Hb}}$ = $^3J_{6\text{-Ha},5}$ = 10.3 Hz, 1 H, 6a-H$_a$), 4.01 (dd, $^3J_{3,4}$ = $^3J_{3,2}$ = 9.2 Hz 1 H, 3a-H), 4.16 (dd, $^2J_{5\text{-Hb},5\text{-Ha}}$ = 12.3, $^3J_{5\text{-Hb},4}$ = 4.4 Hz 1 H, 5b-H$_b$), 4.35 (dd, $^2J_{6\text{-Hb},6\text{-Ha}}$ = 10.3, $^3J_{6\text{-Hb},5}$ = 4.9 Hz, 1 H, 6a-H$_b$), 4.45 (d, $^3J_{1,2}$ = 9.5 Hz, 1 H, 1a-H), 4.79 (d, $^3J_{1,2}$ = 5.5 Hz, 1 H, 1b-H), 4.85 (m, 2 H, 2b-, 4b-H), 5.03 (dd, $^3J_{2,1}$ = $^3J_{2,3}$ = 9.5 Hz, 1 H, 2a-H), 5.09 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 7.1 Hz, 1 H, 3b-H), 5.54 (s, 1 H, PhCH), 7.34 (m, 3 H, Ph), 7.44 (m, 2 H, Ph). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 14.7 (SCH$_2$*C*H$_3$), 20.6–24.0 (3OCO*C*H$_3$), 26.1 (S*C*H$_2$CH$_3$), 28.5 (OCOCH$_2$CH$_2$CO*C*H$_3$), 37.6/34.9 (OCO*C*H$_2$*C*H$_2$COCH$_3$), 61.0 (5b-C), 68.4 (6a-, 4b-C), 70.0 (2b-C), 70.3 (3b-C), 70.9 (5a-C), 72.0 (2a-C), 78.1 (3a-C), 79.2 (4a-C), 84.2 (1a-C), 99.5 (1b-C), 101.1 (Ph*C*H), 125.9–136.9 (6 Ph-C), 169.4/169.8/169.9/171.3 (O*C*OCH$_2$CH$_2$COCH$_3$, 3O*C*OCH$_3$), 206.1 (OCOCH$_2$CH$_2$*C*OCH$_3$). $C_{31}H_{40}O_{14}S$ (668.7): calcd. C 55.68, H 6.03; found C 55.79, H 6.28.

3β-*O*-[(2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-*O*-levulinoyl-β-D-glucopyranosyl]cholesterol (28): Cholesterol (60 mg, 0.160 mmol) and the thio donor **27** (100 mg, 0.150 mmol) were dried thoroughly under high vacuum. Activated 4 Å molecular sieves (900 mg, powder) were added under argon and the mixture was suspended in dry CH_2Cl_2 (6.0 mL). DMTST (100 mg, 0.375 mmol, 2.5 equiv.) was added to the intensively stirred suspension. After stirring overnight, the reaction was quenched with NEt_3 and the solution was directly transferred to flash chromatography (SiO_2, 3×11, PE/EtOAc, 3:1 → 2:1). The crude product was further purified by flash chromatography (SiO_2, 3×13, PE/EtOAc, 3:1 → 2:1) to give the disaccharide saponin **28** (110 mg, 0.111 mmol, 74%). R_f(product) = 0.31 (petroleum ether/ethyl acetate, 2:1). R_f(acceptor) = 0.54 (petroleum ether/ethyl acetate, 2:1). R_f(donor) = 0.15 (petroleum ether/ethyl acetate, 2:1). $[\alpha]_D$ = –2.8 (*c* = 0.06, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.64 (s, 3 H, 18′-H), 0.85 (d, $^3J_{26'/27',25'}$ = 6.6 Hz, 6 H, 26′-, 27′-H), 0.87 (d, $^3J_{21',20'}$ = 6.6 Hz, 3 H, 21′-H), 1.12 (s, 3 H, 19′-H), 1.25–1.70 (m, 21 H), 1.79–1.97 (m, 14 H, 2′-, 7′-, 8′-H, 3 H$_3$CCO), 2.14 (m, 5 H, 4′-H, *H*$_3$CCOCH$_2$CH$_2$CO), 2.56 (t, ^3J = 6.6 Hz, 2 H, H$_3$CCOCH$_2$C*H*$_2$CO), 2.74 (m, 2 H, H$_3$CCOC*H*$_2$CH$_2$CO), 3.22 (dd, $^2J_{5\text{-Ha},5\text{-Hb}}$ = 12.6, $^3J_{5\text{-Ha},4}$ = 7.2 Hz, 1 H, 5b-H$_a$), 3.35–3.40 (m, 2 H, 5a-, 3′-H), 3.57 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 9.1 Hz, 1 H, 4a-H), 3.71 (dd, $^2J_{6\text{-Ha},6\text{-Hb}}$ = $^3J_{6\text{-Ha},5}$ = 10.2 Hz, 1 H, 6a-H$_a$), 3.89 (dd, $^3J_{3,4}$ = $^3J_{3,2}$ = 9.1 Hz, 1 H, 3a-H), 4.09 (dd, $^2J_{5\text{-Hb},5\text{-Ha}}$ = 12.3, $^3J_{5\text{-Hb},4}$ = 4.3 Hz, 1 H, 5b-H$_b$), 4.25 (dd, $^2J_{6\text{-Hb},6\text{-Ha}}$ = 10.5, $^3J_{6\text{-Hb},5}$ = 4.9 Hz, 1 H, 6a-H$_b$), 4.48 (d, $^3J_{1,2}$ = 8.6 Hz, 1 H, 1 H, 1a-H), 4.69 (d, $^3J_{1,2}$ = 5.4 Hz, 1 H, 1b-H), 4.75 (dd, $^3J_{2,3}$ = 6.3, $^3J_{2,1}$ = 5.4 Hz, 1 H, 2b-H), 4.78 (m, 1 H, 4b-H), 4.90 (dd, $^3J_{2,3}$ = $^3J_{2,1}$ = 8.6 Hz, 1 H, 2a-H), 5.01 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 7.0 Hz, 1 H, 3b-H), 5.21 (d, $^3J_{6',7'}$ = 4.6 Hz, 1 H, 6′-H), 5.47 (s, 1 H, PhCH), 7.18–7.4 (m, 5 H, Ph). ^{13}C NMR (151 MHz, $CDCl_3$, selected data, ppm): δ = 61.1 (5b-C), 66.6 (5a-C), 68.5 (4b-C), 68.8 (6a-C), 69.9 (2b-C), 70.2 (3b-C), 73.8 (2a-C), 77.4 (3a-C), 79.1 (4a-C), 79.7 (3′-C), 99.3 (1b-C), 100.0 (1a-C), 101.3 (Ph*C*H), 122.2 (6′-C), 125.9–129.0 (6 Ph-C), 140.2 (5′-C). FAB-MS (positive Mode, Matrix NBA, THF): 1015 [*M* + Na]$^+$. $C_{56}H_{80}O_{15}$ (993.2): calcd. C 67.72, H 8.12; found C 68.34, H 8.50.

3β-*O*-[(2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl)-(1→3)-4,6-*O*-benzylidene-β-D-glucopyranosyl]cholesterol (29): The levulinoylated compound **28** (22 mg, 25 μmol) was dissolved in dichloromethane/methanol (10:1, 2.2 mL) and hydrazinium acetate (200 μL of a 0.21 M solution in methanol, 40 μmol) was added. After 2 h the deprotection was nearly complete (TLC: PE/EtOAc, 2:1) and the excess of NH_2NH_2·HOAc was captured by adding a few drops of acetone. The solvents were removed and the residue chromatographed (SiO_2, 2×6, petroleum ether/ethyl acetate, 3:1) to give the deprotected compound **29** (15 mg, 16 μmol, 64%). R_f(product) = 0.51 (petroleum ether/ethyl acetate, 2:1). R_f(starting material) = 0.44 (petroleum ether/ethyl acetate, 2:1). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.67 (s, 3 H, 18′-H), 0.85 (2d, $^3J_{26'/27',25'}$ = 2.4 Hz, 6 H, 26′-, 27′-H), 0.87 (d, $^3J_{21',20'}$ = 6.0 Hz, 3 H, 21′-H), 1.00 (s, 3 H, 19′-H), 1.07–1.62 (m, 21 H), 1.79–1.97 (m, 14 H, 2′-, 7′-, 8′-H, 3 H$_3$CCO), 2.24–2.40 (m, 2 H, 4′-H), 2.51 (s, 1 H, OH), 3.25 (dd, $^2J_{5\text{-Ha},5\text{-Hb}}$ = 12.1, $^3J_{5\text{-Ha},4}$ = 7.8 Hz, 1 H, 5b-H$_a$), 3.41 (m, 1 H, 5a-H), 3.52 (dd, $^3J_{2,3}$ = $^3J_{2,1}$ = 8.2 Hz, 1 H, 2a-H), 3.60 (m, 2 H, 4a-, 3′-H), 3.77 (dd, $^2J_{6\text{-Ha},6\text{-Hb}}$ = $^3J_{6\text{-Ha},5}$ = 10.2 Hz, 1 H, 6a-H$_a$), 3.83 (dd, $^3J_{3,4}$ = $^3J_{3,2}$ = 9.1 Hz, 1 H, 3a-H), 4.13 (dd, $^2J_{5\text{-Hb},5\text{-Ha}}$ = 12.1, $^3J_{5\text{-Hb},4}$ = 4.8 Hz, 1 H, 5b-H$_b$), 4.25 (dd, $^2J_{6\text{-Hb},6\text{-Ha}}$ = 10.2, $^3J_{6\text{-Hb},5}$ = 4.9 Hz, 1 H, 6a-H$_b$), 4.48 (d, $^3J_{1,2}$ = 7.7 Hz, 1 H, 1 H, 1a-H), 4.90–4.91 (m, 2 H, 1b-, 4b-H), 4.93 (dd, $^3J_{2,1}$ = 6.0, $^3J_{2,3}$ = 7.9 Hz, 1 H, 2b-H), 5.11 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 7.9 Hz, 1 H, 3b-H), 5.27 (dd, $^3J_{6',7'\text{-Ha}}$ = 4.6, $^3J_{6',7'\text{-Hb}}$ = 2.4 Hz, 6′-H), 5.52 (s, 1 H, PhCH), 7.34–7.47 (m, 5 H, Ph) ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 11.8 (18′-CH$_3$), 18.7 (21′-CH$_3$), 19.3 (19′-CH$_3$), 20.7 (3 OCO*C*H$_3$), 21.0 (11′-C), 22.5 (26′-CH$_3$), 22.8 (27′-CH$_3$), 23.8 (23′-C), 24.2 (15′-C), 28.0 (25′-C), 28.2 (12′-C), 29.6 (2′-C), 31.8 (7′-, 8′-C), 35.7 (20′-C), 36.1 (22′-C), 37.2 (10′-C), 37.7 (1′-C), 38.8 (24′-C), 39.5 (16′-C), 39.7 (13′-C), 42.3 (4′-C), 50.1 (9′-C), 56.1 (17′-C), 56.7 (14′-C), 61.9 (5b-C), 66.7 (5a-C), 68.9 (4b-, 6a-C), 71.1 (2b-, 3b-C), 74.5 (2a-C), 79.5 (4a-C, 3′-C), 80.1 (3a-C), 100.6 (1b-C), 101.4 (Ph*C*H), 101.7 (1a-C), 122.3 (6′-C), 125.9 (2 Ph-C), 128.2 (2 Ph-C), 129.0 (1 Ph-C), 137.1 (1 Ph-C), 140.1 (5′-C), 169.8 (3 O*C*OCH$_3$). $C_{51}H_{74}O_{13}$ (895.1). FAB-MS (positive Mode, Matrix NBA + NaI, THF): 917 [*M* + Na]$^+$, 1068 [(*M* + Na*I*)Na]$^+$. MALDI-MS (positive Mode, Matrix DHB, THF): 917.6 [*M* + Na]$^+$, 933.6 [*M* +K]$^+$.

***O*-(2,3,4-Tri-*O*-acetyl-β-D-xylopranosyl)-(1→3)-1,5-anhydro-4,6-*O*-di-*tert*-butylsilandiyl-2-deoxy-D-*arabino*-hex-1-enitol (31):** The protected glucal **30**[43] (500 mg, 1.748 mmol) and the xylosyl trichloroacetimidate **16** (750 mg, 1.784 mmol) were dissolved in dry CH_2Cl_2 (45 mL). The mixture was cooled to –70 °C and activated by the addition of TMSOTf solution (170 μL, 0.01 M in CH_2Cl_2, 1.7 μmol, 0.001 equiv.). The temperature was warmed to –45 °C under thorough TLC control to secure complete conversion of intermediary products. NEt_3 was added dropwise to quench the reac-

tion. The volatiles were evaporated and the crude product was purified by flash chromatography (SiO_2, PE/EtOAc, 5:1 + 0.025% NEt_3). The collected material was lyophilized from chloroform to give the disaccharide glycal **31** (630 mg, 1.158 mmol, 66%). R_f(product) = 0.58 (petroleum ether/ethyl acetate, 2:1). R_f(acceptor) = 0.68 (petroleum ether/ethyl acetate, 2:1). $[\alpha]_D$ = –16.3 (c = 0.2 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.92 (s, 9 H, Si*t*Bu), 1.00 (s, 9 H, Si*t*Bu), 1.99 (s, 3 H, 1 CH_3CO), 2.03 (2s, 6 H, 2 CH_3CO), 3.35 (dd, $^2J_{5\text{-Ha},5\text{-Hb}}$ = 12.2, $^3J_{5\text{-Ha},4}$ = 5.9 Hz, 1 H, 5b-H_a), 3.74 (ddd, $^3J_{5,6\text{-Ha}} = {}^3J_{5,4}$ = 10.4, $^3J_{5,6\text{-Hb}}$ = 4.9 Hz, 1 H, 5a-H), 3.90 (dd, $^2J_{6\text{-Ha},6\text{-Hb}} = {}^3J_{6\text{-Ha},5}$ = 10.4 Hz, 1 H, 6a-H_a), 4.03 (dd, $^3J_{4,5}$ = 10.4, $^3J_{4,3}$ = 7.3 Hz, 1 H, 4a-H), 4.10 (dd, $^2J_{6\text{-Hb},6\text{-Ha}}$ = 10.4, $^3J_{6\text{-Hb},5}$ = 5.0 Hz, 1 H, 6a-H_b), 4.22 (dd, $^3J_{3,4}$ = 7.3, $^3J_{3,2}$ = 1.6 Hz, 1 H, 3a-H), 4.30 (dd, $^2J_{5\text{-Hb},5\text{-Ha}}$ = 12.2, $^3J_{5\text{-Hb},4}$ = 3.9 Hz, 1 H, 5b-H_b), 4.60 (dd, $^3J_{2,1}$ = 6.0, $^3J_{2,3}$ = 1.6 Hz, 1 H, 2a-H), 4.71 (d, $^3J_{1,2}$ = 4.5 Hz, 1 H, 1b-H), 4.77 (dd, $^3J_{2,1}$ = 4.5, $^3J_{2,3}$ = 6.2 Hz, 1 H, 2b-H), 4.81 (ddd, $^3J_{4,3} = {}^3J_{4,5\text{-Ha}}$ = 6.1, $^3J_{4,5\text{-Hb}}$ = 3.9 Hz, 1 H, 4b-H), 5.01 (dd, $^3J_{3,2} = {}^3J_{3,4}$ = 6.2 Hz, 1 H, 3b-H), 6.22 (d, $^3J_{1,2}$ = 6.0 Hz, 1 H, 1a-H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 19.8/20.7/20.8 (3 OCO*C*H_3), 26.8 [SiC(*C*H_3)$_3$], 27.3 [SiC(*C*H_3)$_3$], 60.2 (5b-C), 65.0 (6a-C), 67.9 (4b-C), 69.3 (3b-C), 69.7 (2b-C), 72.4 (5a-C), 74.9 (4a-C), 76.2 (3a-C), 97.8 (1b-C), 100.7 (2a-C), 144.4 (1a-C), 169.3/169.7/169.8 (3 O*C*OCH$_3$). FAB-MS (positive Mode, Matrix NBA + NaI, THF): 567 [M + Na]$^+$. $C_{25}H_{40}O_{11}Si{\cdot}0.4CHCl_3$ (592.4): calcd. C 51.50, H 6.87; found C 51.60, H 7.12.

3β-*O*-[(2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl)-(1→3)-4,6-*O*-di-*tert*-butylsilandiyl-β-D-glucopyranosyl]cholesterol (32): The disaccharide glycal **31** (50 mg, 0.092 mmol) was dissolved in dry CH_2Cl_2 (1.5 mL), cooled in an ice bath and added dropwise with a DMDO solution (1.2 mmol, 0.1 M in acetone, 0.120 mmol). The ice bath was removed and the reaction was raised to room temp. Stirring was continued until all of the starting material was consumed. The volatiles were removed under vacuum at 25 °C. The residue and cholesterol (70 mg, 0.180 mmol) were thoroughly dried together in vacuo. Dry THF (2 mL) was added and the solution was cooled to –60 °C. Then zinc chloride solution (220 μL, 0.5 M in THF, 0.110 mmol) was dropped to the mixture, the cooling bath was removed and stirring was continued for 24 h. The reaction was diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and water. The organic layer was separated and concentrated. Flash chromatographic separation (SiO_2, 3×30, PE/EtOAc, 3:1 → 2:1) of the crude residue yielded the disaccharide saponin **32** (40 mg, 0.042 mmol, 46%). *Note:* replacement of zinc chloride in THF by zinc chloride in Et_2O in some cases led to higher yields. R_f(product) = 0.60 (petroleum ether/ethyl acetate, 2:1). R_f(acceptor) = 0.40 (petroleum ether/ethyl acetate, 2:1). R_f(product) = R_f(acceptor) (petroleum ether/ethyl acetate, 3:1). $[\alpha]_D$ = –3.5 (c = 0.05 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.67 (s, 3 H, 18′-CH_3), 0.85 (2d, $^3J_{26'/27',25'}$ = 2.4 Hz, 6 H, 26′-, 27′-CH_3), 0.87 (d, $^3J_{21',20'}$ = 6.0 Hz, 3 H, 21′-CH_3), 0.99 (s, 12 H, 19′-H, Si*t*Bu), 1.04 (s, 9 H, Si*t*Bu), 1.07–1.62 (m, 21 H), 1.81–1.87 (m, 3 H, 7′-, 8′-H), 1.95–2.01 (m, 2 H, 2′-H), 2.04 (s, 3 H, 1 CH_3CO), 2.07 (2s, 6 H, 2 CH_3CO), 2.26–2.35 (m, 2 H, 4′-H), 2.51 (d, $^3J_{OH,2}$ = 2.5 Hz, 1 H, OH), 3.37–3.39 (m, 2 H, 5a-H, 5b-H_a), 3.44 (ddd, $^3J_{2,OH}$ = 2.5, $^3J_{2,1} = {}^3J_{2,3}$ = 8.8 Hz, 1 H, 2a-H), 3.52 (m, 1 H, 3′-H), 3.56 (dd, $^3J_{3,2} = {}^3J_{3,4}$ = 8.6 Hz, 1 H, 3a-H), 3.81 (dd, $^3J_{4,5} = {}^3J_{4,3}$ = 8.8 Hz, 1 H, 4a-H), 3.90 (dd, $^2J_{6\text{-Ha},6\text{-Hb}} = {}^3J_{6\text{-Ha},5}$ = 10.3 Hz, 1 H, 6a-H_a), 4.13 (dd, $^2J_{6\text{-Hb},6\text{-Ha}}$ = 10.3, $^3J_{6\text{-Hb},5}$ = 5.0 Hz, 1 H, 6a-H_b), 4.38 ($^2J_{5\text{-Hb},5\text{-Ha}}$ = 12.5, $^3J_{5\text{-Hb},4}$ = 4.0 Hz, 1 H, 5b-H_b), 4.40 (d, $^3J_{1,2}$ = 7.9 Hz, 1 H, 1a-H), 4.86 (m, 1 H, 4b-H), 4.90 (dd, $^3J_{2,1}$ = 4.8, $^3J_{2,3}$ = 6.3 Hz, 1 H, 2b-H), 5.00 (d, $^3J_{1,2}$ = 4.6 Hz, 1 H, 1b-H), 5.09 (dd, $^3J_{3,2} = {}^3J_{3,4}$ = 6.5 Hz, 1 H, 3b-H), 5.35 (m, 1 H, 6′-H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 60.7 (5b-C), 66.5 (6a-C), 68.3 (4b-C), 69.6 (3b-C), 70.2 (2b-C), 70.6 (5a-C), 73.9 (2a-C), 75.8 (4a-C), 78.2 (3′-C), 82.8 (3a-C), 100.0 (1b-C), 101.1 (1a-C), 122.1 (6′-C), 140.2 (5′-C), 169.7/169.9/169.7 (3 O*C*OCH$_3$). FAB-MS (positive Mode, Matrix NBA + NaI, THF): 969 [M + Na]$^+$, 1120 [(M + NaI)Na]$^+$. $C_{52}H_{86}O_{13}Si$ (947.3): calcd. C 65.93, H 9.15; found C 66.35, H 9.63.

3β-*O*-{(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→3)]-4,6-*O*-di-*tert*-butylsilandiyl-β-D-glucopyranosyl}cholesterol (33): The disaccharide saponin **32** (70 mg, 0.074 mmol) was dissolved in dry CH_2Cl_2 (1 mL) and treated at room temp. with TMSOTf solution (22 μL, 0.1 M in CH_2Cl_2, 2.2 μmol, 0.03 equiv.). Under vigorous stirring a solution of the galactosyl trichloroacetimidate **13** (75 mg, 0.15 mmol) in dry CH_2Cl_2 (0.5 mL) was added dropwise and the glycosylation progress was followed by TLC (PE/EtOAc, 2:1). After total consumption of the acceptor, the reaction was quenched with NEt_3 and concentrated. Purification by column chromatography (SiO_2, 3×17, PE/EtOAc, 3:1 → 2:1) followed by filtration through BioBeads SX-3 (chloroform) furnished the trisaccharide saponin **33** (85 mg, 0.067 mmol, 91%). R_f(product) = 0.41 (petroleum ether/ethyl acetate, 2:1). R_f(acceptor) = 0.66 (petroleum ether/ethyl acetate, 2:1). $[\alpha]_D$ = –3.6 (c = 0.07 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.67 (s, 3 H, 18′-CH_3), 0.85 (2d, $^3J_{26'/27',25'}$ = 2.4 Hz, 6 H, 26′-, 27′-CH_3), 0.90 (d, $^3J_{21',20'}$ = 6.4 Hz, 3 H, 21′-CH_3), 0.99 (s, 12 H, 19′-H, Si*t*Bu), 1.04 (s, 9 H, Si*t*Bu), 1.07–1.62 (m, 21 H), 1.81–1.87 (m, 3 H, 7′-, 8′-H), 1.95 (s, 3 H, 1 CH_3CO), 1.96–2.04 (m, 5 H, 2′-H, 1 CH_3CO), 2.08 (3s, 9 H, 3 CH_3CO), 2.11 (s, 3 H, 1 CH_3CO), 2.13 (s, 3 H, 1 CH_3CO), 2.26–2.35 (m, 2 H, 4′-H), 3.36 (m, 1 H, 5a-H), 3.46 (m, 2 H, 3′-, 5c-H_a), 3.68 (dd, $^3J_{2,3} = {}^3J_{2,1}$ = 7.4 Hz, 1 H, 2a-H), 3.77 (m, 2 H, 3a, 4a-H), 3.87 (dd, $^2J_{6\text{-Ha},6\text{-Hb}} = {}^3J_{6\text{-Ha},5}$ = 10.3 Hz, 1 H, 6a-H_a), 3.97 (ddd, $^3J_{5,4}$ = 0, $^3J_{5,6\text{-Ha}} = {}^3J_{5,6\text{-Hb}}$ = 6.8 Hz, 1 H, 5b-H), 4.14 (m, 3 H, 6a-H_b, 6b-H_a, 6b-H_b), 4.43 (d, $^3J_{1,2}$ = 7.6 Hz, 1 H, 1a-H), 4.62 (dd, $^2J_{5\text{-Hb},5\text{-Ha}}$ = 12.7, $^3J_{5\text{-Hb},4}$ = 2.5 Hz, 1 H, 5c-H_b), 4.75 (ddd, $^3J_{4,5\text{-Hb}}$ = 2.5, $^3J_{4,5\text{-Ha}} = {}^3J_{4,3} < 1$ Hz, 1 H, 4c-H), 4.90 (d, $^3J_{1,2}$ = 7.8 Hz, 1 H, 1b-H), 4.94 (m, 2 H, 2c-, 3c-H), 5.08 (dd, $^3J_{2,1}$ = 7.9, $^3J_{2,3}$ = 10.2 Hz, 1 H, 2b-H), 5.13 (d, $^3J_{1,2} < 1$ Hz, 1 H, 1c-H), 5.22 (dd, $^3J_{3,2}$ = 10.2, $^3J_{3,4}$ = 3.4 Hz, 1 H, 3b-H), 5.35 (m, 2 H, 4b-, 6′-H). ^{13}C NMR (151 MHz, $CDCl_3$, selected data, ppm): δ = 58.9 (5c-C), 61.3 (6b-C), 66.9 (6a-C), 67.2 (4c-C), 67.7 (4b-C), 68.0 (2c-, 3c-C), 70.5 (5a-C), 70.8 (5b-, 2b-C), 70.9 (3b-C), 76.1 (4a-C), 80.1 (3a-C), 80.3 (3′-C), 80.6 (2a-C), 97.4 (1c-C), 99.7 (1b-C), 101.1 (1a-C), 122.2 (6′-C), 140.2 (5′-C), 169.3–170.2 (7 O*C*OCH$_3$). $C_{66}H_{104}O_{22}Si{\cdot}H_2O$ (1294.9): calcd. C 61.22, H 8.25; found C 60.98, H 8.32.

3β-*O*-{β-D-Galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-glucopyranosyl}cholesterol (34): Compound **18** (15 mg, 13 μmol) was dissolved in dry methanol/CH_2Cl_2 (4:1, 1 mL) and treated with solid sodium methoxide (3 mg, 0.055 mmol). After 3 h the starting material was completely consumed. The solution was neutralized with IR-120 (H^+), filtered and concentrated to give the completely deprotected trisaccharide saponin **34** (10 mg, 12 μmol, qu) as white solid. R_f(product) = 0.47 ($CHCl_3$/MeOH/H_2O, 60:35:8). ^{1}H NMR (600 MHz, $CDCl_3$/MeOD/D_2O, 60:35:2, ppm): δ = 0.65 (s, 3 H, 18′-CH_3), 0.84 (2d, $^3J_{26'/27',25'}$ = 2.4 Hz, 6 H, 26′-, 27′-CH_3), 0.90 (d, $^3J_{21',20'}$ = 6.4 Hz, 3 H, 21′-CH_3), 0.98 (s, 3 H, 19′-CH_3), 1.07–1.62 (m, 21 H), 1.81–1.99 (m, 5 H, 2′-, 7′-, 8′-H), 2.25–2.35 (m, 2 H, 4′-H), 3.24–3.26 (m, 3 H, 4a-, 5a-, 2c-H), 3.34 (dd, $^3J_{3,2} = {}^3J_{3,4}$ = 9.1 Hz, 1 H, 3c-H), 3.43 (dd, $^3J_{4,3} = {}^3J_{4,5}$ = 8.9 Hz, 1 H, 4a-H), 3.49–3.53 (m, 4 H, 2b-, 3b-, 5b-, 4c-H), 3.57 (m, 1 H, 3′-H), 3.60 (m, 2 H, 2a-, 3a-H), 3.69–3.80 (m, 4 H, 6a-H_a, 6a-H_b, 6b-H_a, 6b-H_b), 3.88 (dd, $^3J_{4,3}$ = 1, $^3J_{4,5} < 1$ Hz, 1 H, 4b-H), 3.90 (dd, $^2J_{5\text{-Hb},5\text{-Ha}}$ = 11.4, $^3J_{5\text{-Hb},4}$ = 5.3 Hz, 1 H, 5c-H_b), 4.50–4.51 (m, 2

H, 1a-, 1c-H), 4.64 (d, $^3J_{1,2}$ = 7.1 Hz, 1b-H), 5.34 (s, 1 H, 6′-H). ^{13}C NMR (151 MHz, $CDCl_3$/MeOD/D_2O, 60:35:2, ppm): δ = 12.2 (18′-CH_3), 19.1 (21′-CH_3), 19.6 (19′-CH_3), 21.5 (11′-C), 22.9 (26′-CH_3), 23.1 (27′-CH_3), 24.3 (23′-C), 24.7 (15′-C), 28.5 (25′-C), 28.7 (12′-C), 30.0 (2′-C), 32.4 (7′-, 8′-C), 36.3 (20′-C), 36.7 (22′-C), 37.2 (10′-C), 37.7 (1′-C), 39.0 (24′-C), 40.0 (16′-C), 40.3 (13′-C), 43.0 (4′-C), 50.7 (9′-C), 56.7 (17′-C), 57.3 (14′-C), 61.7 (6b-C), 62.0 (6a-C), 66.7 (5c-C), 69.1 (4a-C), 69.4 (4b-C), 70.1 (4c-C), 72.8 (2b-C), 73.8 (3b-C), 74.2 (2c-C), 75.8 (5b-C), 76.3 (5a-C), 77.2 (3c-C), 80.5 (3′-C, 2a-C), 86.1 (3a-C), 101.2 (1a-C), 104.1 (1b-C), 104.5 (1c-C), 122.5 (6′-C), 140.9 (5′-C). $C_{44}H_{74}0_{15}$ (843.0). MALDI-MS (positive Mode, Matrix DHB, MeOH): 865.1 [M + Na]$^+$. FAB-MS (positive Mode, Matrix NBA, THF): 865 [M + Na]$^+$.

3β-*O*-{(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→3)]-6-*O*-sulfo-β-D-glucopyranosyl}cholesterol (35): The trisaccharide saponin **18** (30 mg, 0.026 mmol) was dissolved in pyridine (1 mL). Sulfur trioxide–pyridine complex (5 mg, 0.031 mmol) was added and the reaction mixture was stirred overnight. Methanol was added to quench the reaction, followed by water and dichloromethane. The organic solvents were removed and the crude product purified by flash chromatography (SiO_2, 2 × 5, CH_2Cl_2/MeOH, 10:1) to give the sulfated saponin **35** (11 mg, 9.0 μmol, 35%). R_f(product) = 0.08 (chloroform/methanol, 10:1). ^{1}H NMR (250 MHz, $CDCl_3$ + 2 drops MeOD, ppm): δ = 0.60 (s, 3 H, 18′-CH_3), 0.78 (d, $^3J_{26'/27',25'}$ = 6.6 Hz, 6 H, 26′-, 27′-CH_3), 0.83 (d, $^3J_{21',20'}$ = 6.4 Hz, 3 H, 21′-CH_3), 0.93 (s, 3 H, 19′-CH_3), 1.07–1.60 (m, 21 H), 1.75–2.25 (m, 28 H, 2′-, 4′-, 7′-, 8′-H, 7 CH_3CO), 3.31–3.56 (m, 5 H, 2a-, 4a-, 5a-, 3′-H, 5c-H_a), 3.73 (dd, $^3J_{3,4}$ = $^3J_{3,2}$ = 9.0 Hz, 1 H, 3a-H), 3.90 (ddd, $^3J_{5,4}$ = 0, $^3J_{5,6\text{-Ha}}$ = $^3J_{5,6\text{-Hb}}$ = 6.7 Hz, 1 H, 5b-H), 4.07 (m, 2 H, 6b-H_a, 6b-H_b), 4.15–4.25 (m, 3 H, 6a-H_a, 6a-H_b, 5c-H_b), 4.42 (d, $^3J_{1,2}$ = 7.2 Hz, 1 H, 1a-H), 4.83–4.95 (m, 4 H, 1b-, 1c-, 2c-, 4c-H), 5.02–5.12 (m, 3 H, 2b-, 3b-, 3c-H), 5.35 (m, 2 H, 4b-H, 6′-H).

3β-*O*-{β-D-Galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-6-*O*-sulfo-β-D-glucopyranosyl}cholesterol (36): The acetylated saponin **35** (5 mg, 4.1 μmol) was dissolved in methanol/dichloromethane (1:1, 2 mL) and treated with sodium methoxide (1 mg). After complete deprotection the solution was neutralized with IR-120 (H^+), filtered through IR-120 (Na^+) and the solvents evaporated. Lyophilisation from dioxane/water gave the sodium salt as colourless lyophilisate **36** (3.5 mg, 3.7 μmol, 90%). R_f(product, free acid) = 0.31 (ethyl acetate/2-propanol/water, 9:4:2). ^{1}H NMR (250 MHz, $CDCl_3$/MeOD/D_2O, 65:35:3, ppm): δ = 0.42 (s, 3 H, 18′-CH_3), 0.60 (d, $^3J_{26'/27',25'}$ = 6.6 Hz, 6 H, 26′-, 27′-CH_3), 0.65 (d, $^3J_{21',20'}$ = 6.3 Hz, 3 H, 21′-CH_3), 0.74 (s, 3 H, 19′-CH_3), 0.78–1.29 (m, 21 H), 1.56–2.09 (m, 7 H, 2′-, 4′-, 7′-, 8′-H), 2.99–4.35 (m, 21 H, 1a-, 2a-, 3a-, 4a-, 5a-, 1b-, 2b-, 3b-, 4b-, 5b-, 3′-, 1c-, 2c-, 3c-, 4c-H, 5c-H_a, 5c-H_b, 6b-H_a, 6b-H_b, 6a-H_a, 6a-H_b), 5.11 (br. s, 1 H, 6′-H).

3β-*O*-{(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→3)]-6-*O*-dodecylcarbamoyl-β-D-glucopyranosyl}cholesterol (37): The trisaccharide saponin **18** (60 mg, 0.053 mmol) was dissolved in pyridine (2 mL). Dodecyl isocyanate (12 mg, 0.055 mmol) was added and the reaction mixture was stirred at 80–100 °C overnight. To complete the reaction further portions of dodecyl isocyanate (3 × 2.2 mg) were added to the hot reaction mixture. Then the pyridine was evaporated and the residue purified by flash chromatography (SiO_2, 2 × 12, PE/EtOAc, 2:1 → 1:1) to give the carbamoyl compound **37** (60 mg, 0.044 mmol, 84%). R_f(product) = 0.43 (petroleum ether/ethyl acetate, 1:1). $[\alpha]_D$ = –1.8 (c = 0.05 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.67 (s, 3 H, 18′-CH_3), 0.85 (2d, $^3J_{26'/27',25'}$ = 2.6 Hz, 6 H, 26′-, 27′-CH_3), 0.87 (t, $^3J_{12'',11''}$ = 6.8 Hz, 3 H, 12′′-CH_3), 0.90 (d, $^3J_{21',20'}$ = 6.4 Hz, 3 H, 21′-CH_3), 1.00 (s, 3 H, 19′-CH_3), 1.07–1.62 (m, 41 H), 1.81–1.87 (m, 3 H, 7′-, 8′-H), 1.97 (s, 3 H, 1 CH_3CO), 2.03–2.04 (m, 11 H, 2′-H, 3 CH_3CO), 2.09 (3s, 3 H, 1 CH_3CO), 2.11 (s, 3 H, 1 CH_3CO), 2.16 (s, 3 H, 1 CH_3CO), 2.31–2.33 (m, 2 H, 4′-H), 3.14 (m, 3 H, CONHCH_2CH$_2$, OH), 3.32 (m, 1 H, 5a-H), 3.40 (m, 2 H, 4a-H, 5c-H_a), 3.51 (m, 1 H, 3′-H), 3.61 (dd, $^3J_{2,3}$ = $^3J_{2,1}$ = 7.9 Hz, 1 H, 2a-H), 3.75 (dd, $^3J_{3,4}$ = $^3J_{3,2}$ = 8.8 Hz, 1 H, 3a-H), 3.91 (ddd, $^3J_{5,4}$ = 0, $^3J_{5,6\text{-Ha}}$ = $^3J_{5,6\text{-Hb}}$ = 6.7 Hz, 1 H, 5b-H), 4.13 (m, 2 H, 6b-H_a, 6b-H_b), 4.21 (dd, $^2J_{6\text{-Ha},6\text{-Hb}}$ = 11.7, $^3J_{6\text{-Ha},5}$ = 1.0 Hz, 1 H, 6a-H_a), 4.26 (dd, $^2J_{5\text{-Hb},5\text{-Ha}}$ = 11.8, $^3J_{5\text{-Hb},4}$ = 4.4 Hz, 1 H, 5c-H_b), 4.41 (dd, $^2J_{6\text{-Hb},6\text{-Ha}}$ = 11.7, $^3J_{6\text{-Hb},5}$ = 3.9 Hz, 1 H, 6a-H_b), 4.49 (d, $^3J_{1,2}$ = 7.4 Hz, 1 H, 1a-H), 4.74 (s, 1 H, CONHCH$_2$), 4.87 (d, $^3J_{1,2}$ = 7.8 Hz, 1 H, 1b-H), 4.89 (d, $^3J_{1,2}$ = 6.0 Hz, 1 H, 1c-H), 4.94 (m, 2 H, 2c-, 4c-H), 5.04 (dd, $^3J_{3,2}$ = 10.3, $^3J_{3,4}$ = 2.9 Hz, 1 H, 3b-H), 5.13 (dd, $^3J_{2,3}$ = 10.3, $^3J_{2,1}$ = 7.8 Hz, 1 H, 2b-H), 5.16 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 7.9 Hz, 1 H, 3c-H), 5.35 (s, 1 H, 6′-H), 5.37 (dd, $^3J_{4,3}$ = 2.8, $^3J_{4,5}$ < 1 Hz, 1 H, 4b-H). ^{13}C NMR (151 MHz, $CDCl_3$, selected data, ppm): δ = 61.4 (6b-C), 61.8 (5c-C), 63.7 (6a-C), 67.1 (4b-C), 68.6 (4c-C), 68.7 (4a-C), 70.0 (2b-C), 70.8 (2c-, 3c-, 5b-C), 71.0 (3b-C), 74.0 (5a-C), 79.2 (2a-C), 79.9 (3′-C), 82.8 (3a-C), 99.1 (1b-C), 99.6 (1c-C), 100.1 (1a-C), 122.5 (6′-C), 140.9 (5′-C), 156.6 (OCONH), 169.3–170.2 (7 OCOCH$_3$). $C_{71}H_{113}NO_{23}$ (1348.6). MALDI-MS (positive Mode, Matrix DHB, THF): 1386.8 [M + K]$^+$. FAB-MS (positive Mode, Matrix NBA, THF): 1370 [M + Na]$^+$.

3β-*O*-{β-D-Galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-6-*O*-dodecylcarbamoyl-β-D-glucopyranosyl}cholesterol (38): The acetylated saponin **37** (10 mg, 7.4 μmol) was dissolved in methanol/dichloromethane (1:2, 3 mL) and treated with sodium methoxide (1 mg). After complete deprotection the solution was neutralized with IR-120 (H^+), evaporated and the residue filtered through a short pad of silica gel (EtOAc/MeOH/H_2O, 9:5:2) to obtain the C_{12}-elongated neosaponin **38** (5 mg, 4.7 μmol, 64%), which was lyophilized from dioxane/water. R_f(product, free acid) = 0.49 (ethyl acetate/2-propanol/water, 9:4:2). ^{1}H NMR (250 MHz, $CDCl_3$/MeOD/D_2O, 65:35:3, ppm): δ = 0.43 (s, 3 H, 18′-CH_3), 0.61–0.72 (m, 12 H, 12′′-, 21′-, 26′-, 27′-CH_3), 0.75 (s, 3 H, 19′-CH_3), 0.86–1.57 (m, 43 H), 1.65–1.79 (m, 3 H, 7′-, 8′-H), 2.05 (m, 2 H, 4′-H), 2.80–3.51 (m, 19 H, CONHCH_2CH$_2$, 2a-, 3a-, 4a-, 5a-H, 6a-H_a, 6a-H_b, 2b-, 3b-, 5b-H, 6b-H_a, 6b-H_b, 2c-, 3c-, 4c-, 5c-H_a, 5c-H_b, 3′-H), 3.66 (dd, $^3J_{4,3}$ = 1, $^3J_{4,5}$ < 1 Hz, 1 H, 4b-H), 3.95–4.50 (m, 4 H, 1a-, 1b-, 1c-H, CONHCH$_2$), 5.11 (d, ^3J = 4.0 Hz, 6′-H).

3β-*O*-{(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)-4,6-*O*-benzylidene-β-D-glucopyranosyl}cholestanol (39): A solution of the benzylated cholesterol saponin **23** (140 mg, 0.122 mmol) in ethanol/dichloromethane (2:1, 15 mL) was stirred with Pd/C (30 mg, 10% Pd), acetic acid (0.5 mL) and formic acid (50 μL) under hydrogen atmosphere for 48 h. TLC (R_f = 0.13, toluene/acetone, 1:1) indicated complete deprotection. The catalyst was filtered off and the solvents were evaporated. The residue was codestilled with toluene, dried, dissolved in acetonitrile (4 mL) and treated with benzaldehyde dimethyl acetal (25 μL, 0.150 mmol). The solution was acidified with p-toluenesulfonic acid and stirred overnight. NEt_3 was added and the mixture concentrated. The residue was separated by flash chromatography (SiO_2, PE/EtOAc, 4:1 → 2:1) to give the benzylidenated cholestanol **39** (90 mg, 0.093 mmol, 76% over 2 steps). R_f(product) = 0.24 (petroleum ether/ethyl acetate, 2:1). $[\alpha]_D$ = –1.0 (c = 0.078 in $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 0.62 (s, 3 H, 18′-H), 0.79–0.83 (2d, $^3J_{26'/27',25'}$ < 1 Hz, 6 H, 26′-, 27′-H), 0.85–0.89 (m, 6 H, 19′-, 21′-H), 0.93–1.64 (m, 24 H), 1.70–2.13 (m, 19 H, 2′-, 4′-, 7′-, 8′-, 4 H_3CCO), 2.70 (s, 1 H, OH), 3.35 (m, 1 H, 5a-H), 3.49–3.68 (m, 3 H, 2a-, 4a-, 3′-H), 3.75–3.82 (m, 2 H, 6a-H_a, 3a-H), 3.93 (m, 1 H, 5b-H), 4.12 (m, 2 H, 6b-H_a,

6b-H_b), 4.30 (dd, $^2J_{6\text{-Hb},6\text{-Ha}}$ = 10.5, $^3J_{6\text{-Hb},5}$ = 5.0 Hz, 1 H, 6a-H_b), 4.61 (d, $^3J_{1,2}$ = 7.5 Hz, 1 H, 1a-H), 4.89 (d, $^3J_{1,2}$ = 7.9 Hz, 1 H, 1b-H), 5.01 (dd, $^3J_{3,2}$ = 10.5, $^3J_{3,4}$ = 3.3 Hz, 1 H, 3b-H), 5.22 (dd, $^3J_{2,3}$ = 10.6, $^3J_{2,1}$ = 7.9 Hz, 1 H, 2b-H), 5.37 (dd, $^3J_{4,3}$ = 3.1, $^3J_{4,5}$ < 1 Hz, 1 H, 4b-H), 5.50 (s, 1 H, PhCH), 7.31–7.48 (m, 5 H, 1 Ph). FAB-MS (positive Mode, Matrix NBA, THF): 991 [M + Na]$^+$. $C_{54}H_{80}O_{15}$·0.5H_2O (978.2): calcd. C 66.30, H 8.35; found C 66.11, H 8.52.

3β-*O*-{(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→3)]-4,6-*O*-benzylidene-β-D-glucopyranosyl}cholestanol (41): The disaccharide saponin **39** (200 mg, 0.207 mmol) and the trichloroacetimidate **40**[46] (150 mg, 0.248 mmol) were dissolved in CH_2Cl_2 (5 mL). TMSOTf (200 μL of 0.1 M solution in CH_2Cl_2, 0.020 mmol, 0.01 equiv.) was added. After 20 min the reaction was quenched with NEt_3 and concentrated. The residue was separated by column chromatography (SiO_2, 10 g, PE/EtOAc, 8:1 → 4:1) to yield the trisaccharide saponin **41** (220 mg, 0.156 mmol, 75%). R_f(donor) = 0.80 (toluene/acetone, 10:1). R_f(acceptor) = 0.075 (toluene/acetone, 10:1). R_f(product) = 0.55 (toluene/acetone, 10:1). R_f(product) = 0.30 (petroleum ether/ethyl acetate, 3:1). $[\alpha]_D$ = –5.6 (c = 0.1 in $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 0.62 (s, 3 H, 18′-H), 0.79 (s, 3 H, 19′-H), 0.79–0.83 (2d, $^3J_{26'/27',25'}$ = 2 Hz, 6 H, 26′-, 27′-H), 0.88 (d, $^3J_{21',20'}$ = 8.6 Hz, 3 H, 21′-H), 0.93–1.60 (m, 24 H), 1.64–2.13 (m, 19 H, 2′-, 4′-, 7′-, 8′-, 4 H_3CCO), 3.38–3.83 (m, 6 H, 2a-, 4a-, 5a-, 3′-H, 6a-H_a, 5c-H_a), 3.96 (m, 1 H, 5b-H), 4.06–4.20 (m, 3 H, 6b-H_a, 6b-H_b, 3a-H), 4.34 (dd, $^2J_{6\text{-Hb},6\text{-Ha}}$ = 10.5, $^3J_{6\text{-Hb},5}$ = 4.6 Hz, 1 H, 6a-H_b), 4.48 (d, $^3J_{1,2}$ = 7.3 Hz, 1 H, 1a-H), 4.74 (dd, $^2J_{5\text{-Hb},5\text{-Ha}}$ = 11.8, $^3J_{5\text{-Hb},4}$ = 1.5 Hz, 1 H, 5c-H_b), 4.93–5.07 (m, 3 H, 1b-, 2b-, 1c-H), 5.19 (dd, $^3J_{3,2}$ = 10.1, $^3J_{3,4}$ = 3.3 Hz, 1 H, 3b-H), 5.33 (ddd, $^3J_{4,3}$ = $^3J_{4,5\text{-Ha}}$ = 3.3, $^3J_{4,5\text{-Hb}}$ = 1.5 Hz, 1 H, 4c-H), 5.36 (dd, $^3J_{2,3}$ = $^3J_{2,1}$ = 3.0 Hz, 1 H, 2c-H), 5.44 (dd, $^3J_{4,3}$ = 3.3, $^3J_{4,5}$ < 1 Hz, 1 H, 4b-H), 5.49 (m, 2 H, 3c-H, PhCH), 7.09–8.11 (m, 20 H, 4 Ph). $C_{80}H_{100}O_{22}$ (1413.6): calcd. C 67.97, H 7.13; found C 67.90, H 7.31.

3β-*O*-{2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→2)-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→3)]-β-D-glucopyranosyl}-cholestanol (42). a) The trisaccharide saponin **41** (190 mg, 0.135 mmol) was dissolved in ethanol/dioxane (3.33:1, 6.5 mL). $Pd(OH)_2$/C (40 mg, 20%) and Pd/C (10 mg, 10%) were suspended in the solution. Acetic acid (750 μL) was added and the reaction mixture was stirred overnight. The catalyst was filtered off, the solvents were removed and the residue was purified by flash chromatography (SiO_2, 8 g, PE/EtOAc, 3:1 → 2:1) to afford the debenzylidenated saponin **42** (120 mg, 0.090 mmol, 67%).

b) Alternative deprotection: The benzylidenated compound **41** (60 mg, 0.042 mmol), ethanthiol (15 μL) and *p*-toluenesulfonic acid (2 mg) were stirred in CH_2Cl_2 (0.5–1 mL). After complete deprotection, NEt_3 was added and the mixture was concentrated. Flash chromatography (SiO_2, 10 g, PE/EtOAc, 4:1 → 2:1) led to the deprotected saponin **42** (50 mg, 0.037 mmol, 88%). R_f(product) = 0.41 (petroleum ether/ethyl acetate, 1:1). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ = 0.60 (s, 3 H, 18′-H), 0.75 (s, 3 H, 18′-H), 0.82–0.84 (2d, $^3J_{26'/27',25'}$ = 2 Hz, 6 H, 26′-, 27′-H), 0.87 (d, $^3J_{21',20'}$ = 7.9 Hz, 3 H, 21′-H), 0.93–1.60 (m, 24 H), 1.64–2.13 (m, 19 H, 2′-, 4′-, 7′-, 8′-, 4 H_3CCO), 2.75 (ddd, $^3J_{5,6\text{-Ha}}$ = $^3J_{5,6\text{-Hb}}$ = 6.7, $^3J_{5,4}$ < 1 Hz, 1 H, 5b-H), 3.33 (m, 1 H, 5a-H), 3.45 (m, 1 H, 3′-H), 3.54–3.98 (m, 8 H, 2a-, 3a-, 4a-, 6a-H_a, 6a-H_b, 6b-H_a, 6b-H_b, 5c-H_a), 4.38 (d, $^3J_{1,2}$ = 7.3 Hz, 1 H, 1a-H), 4.51 (d, $^3J_{1,2}$ = 7.8 Hz, 1 H, 1b-H), 4.58 (dd, $^2J_{5\text{-Hb},5\text{-Ha}}$ = 12.2, $^3J_{5\text{-Hb},4}$ = 4.6 Hz, 1 H, 5c-H_b), 4.74 (dd, $^3J_{3,2}$ = 10.5, $^3J_{3,4}$ = 3.5 Hz, 1 H, 3b-H), 4.98–5.05 (m, 3 H, 1c-, 2b-, 4b-H), 5.33 (ddd, $^3J_{4,3}$ = $^3J_{4,5\text{-Ha}}$ = 7.8, $^3J_{4,5\text{-Hb}}$ = 4.6 Hz, 1 H, 4c-H), 5.51 (dd, $^3J_{2,1}$ = 5.8, $^3J_{2,3}$ = 7.8 Hz, 1 H, 2c-H), 5.82 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 7.8 Hz, 1 H, 3c-H), 7.30–7.98 (m, 15 H, 3Ph). MALDI-MS (positive Mode, Matrix DHB, THF): 1348.0 [M + Na]$^+$, 1364.3 [M + K]$^+$. FAB-MS (positive Mode, Matrix NBA, THF): 1347 [M + Na]$^+$. $C_{73}H_{96}O_{22}$·H_2O (1343.5): calcd. C 65.25, H 7.35; found C 65.18, H 7.68.

3β-*O*-{(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→3)]-β-D-glucuronopyranosyl}-cholestanol (43): The debenzylidenated trisaccharide saponin **42** (100 mg, 76 μmol), TEMPO (2.7 mg) and tetrabutylammonium bromide (80 mg, 230 μmol) were dissolved in CH_2Cl_2/saturated $NaHCO_3$ solution (5:3, 8 mL). The reaction mixture was cooled to 0 °C and a solution of sodium hypochlorite (80 μL, 380 μmol) in saturated $NaHCO_3$ solution/saturated NaCl solution (1:3, 4.5 mL) was added. Ice cooling was removed and the temperature was raised to room temp. Further two portions of the NaOCl solution (100 μL, 460 μmol) were added. After 30 min the starting material had completely disappeared (TLC: $CHCl_3$/MeOH, 10:1 or EtOAc/*i*PrOH/H_2O, 9:4:2). The reaction mixture was diluted with CH_2Cl_2 (50 mL), the organic phase was separated and the solvents evaporated. Repeated flash chromatography (SiO_2, 30 g, toluene/acetone, 1:1 → 1:3 followed by SiO_2, 10 g, $CHCl_3$/CH_3OH, 20:1) gave the glucuronic acid saponin **43** (70 mg, 52 μmol, 68%). R_f(product) = 0.48 (toluene/acetone, 1:3). ^{1}H NMR (600 MHz, $CDCl_3$/MeOD, 10:1, ppm): δ = 0.60 (s, 3 H, 18′-H), 0.75–0.82 (2d, $^3J_{26'/27',25'}$ < 1 Hz, 6 H, 26′-, 27′-H), 0.84–0.87 (m, 6 H, 19′-, 21′-H), 0.93–2.13 (m, 43 H, 4 H_3CCO), 3.37 (s, 1 H, OH), 3.57 (m, 1 H, 3′-H), 3.66 (m, 2 H, 2a-, 5b-H), 3.77 (m, 2 H, 4a-, 5a-H), 3.81 (dd, $^2J_{5\text{-Ha},5\text{-Hb}}$ = 12.9, $^3J_{5\text{-Ha},4}$ = 4.2 Hz, 1 H, 5c-H_a), 3.94 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 8.8 Hz, 1 H, 3a-H), 4.04 (dd, $^2J_{6\text{-Ha},6\text{-Hb}}$ = 11.1, $^3J_{6\text{-Ha},5}$ = 5.9 Hz, 1 H, 6b-H_a), 4.09 (dd, $^2J_{6\text{-Hb},6\text{-Ha}}$ = 11.1, $^3J_{6\text{-Hb},5}$ = 7.8 Hz, 1 H, 6b-H_b), 4.49 (d, $^3J_{1,2}$ = 7.2 Hz, 1 H, 1a-H), 4.85 (d, $^3J_{1,2}$ = 7.1 Hz, 1 H, 1b-H), 5.00 (dd, $^2J_{5\text{-Hb},5\text{-Ha}}$ = 12.9, $^3J_{5\text{-Hb},4}$ = 3.0 Hz, 1 H, 5c-H_b), 5.06 (m, 2 H, 2b-, 3b-H), 5.24 (ddd, $^3J_{4,3}$ = $^3J_{4,5\text{-Ha}}$ = 4.3, $^3J_{4,5\text{-Hb}}$ = 3.0 Hz, 1 H, 4c-H), 5.33 (d, $^3J_{1,2}$ = 2.9 Hz, 1 H, 1c-H), 5.36 (dd, $^3J_{4,3}$ = 3.0, $^3J_{4,5}$ < 1 Hz, 1 H, 4b-H), 5.39 (dd, $^3J_{2,1}$ = 2.9, $^3J_{2,3}$ = 4.4 Hz, 1 H, 2c-H), 5.66 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 4.4 Hz, 1 H, 3c-H), 7.30–7.98 (m, 15 H, 3 Ph). ^{13}C NMR (151 MHz, $CDCl_3$/MeOD, 10:1, selected data, ppm): δ = 59.3 (5c-C), 60.6 (6b-C), 67.0 (4b-C), 67.7 (3c-C), 67.9 (4c-C), 68.2 (2c-C), 69.4 (2b-C), 69.9 (5b-C), 70.0 (4a-C), 70.9 (3b-C), 74.0 (5a-C), 79.2 (2a-C), 79.4 (3′-C), 79.8 (3a-C), 97.3 (1c-C), 99.2 (1b-C), 99.6 (1a-C). $C_{73}H_{94}O_{23}$ (1339.5). FAB-MS (positive Mode, Matrix Glycerine/NBA, 1:1 + NaI, DMSO): 1362 [M + Na]$^+$, 1384 [(M – H)Na + Na]$^+$, 1378 [M + K]$^+$.

3β-*O*-{β-D-Galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-glucuronopyranosyl}cholestanol (1b): Protected glucurono saponin **43** (30 mg, 22 μmol) was dissolved in absolute methanol (20 mL) and treated with a sodium methoxide solution (3 mL of 0.33 M solution in CH_3OH, 1.0 mmol). During stirring overnight the solution became turbid. The reaction was neutralized with ion exchange resin IR-120 (H^+), filtered and the solvents were removed. Flash chromatography of the residue (SiO_2, 9 g, CH_2Cl_2 → $CHCl_3$/CH_3OH, 2:1 → $CHCl_3$/CH_3OH/H_2O, 60:35:8) yielded the deprotected trisaccharide saponin **1b** (9 mg, 10 μmol, 45%). R_f(product) = 0.43 ($CHCl_3$/CH_3OH/H_2O, 60:35:8). ^{1}H NMR (600 MHz, $CDCl_3$/MeOD/D_2O, 60:35:3, ppm): δ = 0.65 (s, 3 H, 18′-CH_3), 0.82 (s, 3 H, 19′-CH_3), 0.86–0.87 (2d, $^3J_{26'/27',25'}$ = 2.5 Hz, 6 H, 26′-, 27′-CH_3), 0.90 (d, $^3J_{21',20'}$ = 6.6 Hz, 3 H, 21′-CH_3), 1.07–1.99 (m, 28 H), 1.61 (m, 1 H, 6′-H_a), 1.69 (m, 1 H, 3′-H_a), 1.84 (m, 1 H, 2′-H_a), 3.25 (dd, $^2J_{5\text{-Ha},5\text{-Hb}}$ = $^3J_{5\text{-Ha},4}$ = 11.1 Hz, 1 H, 5c-H_a), 3.29 (dd, $^3J_{2,1}$ = $^3J_{2,3}$ = 9.1 Hz, 1 H, 2c-H), 3.37 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 9.1 Hz, 1 H, 3c-H), 3.54–3.56 (m, 5 H, 2b-, 3b-, 5b-, 4c-, 5a-H),

3.61 (dd, $^3J_{4,3} = {}^3J_{4,5} = 8.2$ Hz, 1 H, 4a-H), 3.71–3.74 (m, 5 H, 2a-, 3a-, 3′-H, 6b-H_a, 6b-H_b), 3.90 (dd, $^3J_{4,3} = 1.9$, $^3J_{4,5} < 1$ Hz, 1 H, 4b-H), 3.93 (dd, $^2J_{5\text{-Hb},5\text{-Ha}} = 11.1$, $^3J_{5\text{-Hb},4} = 5.4$ Hz, 1 H, 5c-H_b), 4.55 (d, $^3J_{1,2} = 7.2$ Hz, 1 H, 1a-H), 4.65 (d, $^3J_{1,2} = 7.8$ Hz, 1 H, 1c-H), 4.71 (d, $^3J_{1,2} = 7.1$ Hz, 1 H, 1b-H). ^{13}C NMR (151 MHz, $CDCl_3$/MeOD/D_2O, 60:35:3, selected data, ppm): δ = 61.1 (6b-C), 65.8 (5c-C), 68.8 (4b-C), 69.7–72.3 (2b-, 3b-, 5b-, 5a-, 4c-C), 73.9 (2c-C), 76.4 (4a-C), 76.5 (3c-C), 79.8 (2a-, 3a-C), 83.9 (3′-C), 99.9 (1a-C), 103.3 (1b-C), 103.4 (1c-C). $C_{44}H_{74}0_{16}$ (859.1). FAB-MS (positive Mode, Matrix Glycerine/NBA, 1:1 + NaI, THF): 881 [M + Na]$^+$, 903 [(M – H)Na + Na]$^+$.

3β-*O*-{2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→2)-[2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)]-4,6-benzylidene-β-D-glucopyranosyl}cholestanol (45): The disaccharide saponin **39** (100 mg, 0.103 mmol) and the rhamnosyl trichloroacetimidate **44**[49] (70 mg, 0.155 mmol) were dissolved in CH_2Cl_2 (3 mL). TMSOTf (50 μL of 0.02 M solution in CH_2Cl_2, 1 μmol, 0.01 equiv.) was added. After 20 min the reaction was quenched with NEt_3 and concentrated. The residue was purified by column chromatography (SiO_2, 2×15, PE/EtOAc, 3:1 → 2:1) to obtain the trisaccharide saponin **45** (120 mg, 0.097 mmol, 94%). R_f(product) = 0.61 (petroleum ether/ethyl acetate, 1:1) = R_f(acceptor) = R_f(donor). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.65 (s, 3 H, 18′-CH_3), 0.74 (d, $^3J_{6,5}$ = 6.1 Hz, 3 H, 6c-CH_3), 0.82 (s, 3 H, 19′-CH_3), 0.86–0.87 (2d, $^3J_{26'/27',25'} = 2.5$ Hz, 6 H, 26′-, 27′-CH_3), 0.90 (d, $^3J_{21',20'} = 6.6$ Hz, 3 H, 21′-CH_3), 1.07–2.14 (m, 52 H, 7 H_3CCO + 31 cholestanol H), 3.39 (m, 1 H, 5a-H), 3.55 (dd, $^3J_{4,5} = {}^3J_{4,3} = 9.3$ Hz, 1 H, 4a-H), 3.57 (m, 1 H, 3′-H), 3.74 (m, 2 H, 2a-H, 6a-H_a), 3.92 (dd, $^3J_{3,4} = {}^3J_{3,2} = 9.1$ Hz, 1 H, 3a-H), 3.96 (ddd, $^3J_{5,4} = 0$, $^3J_{5,6\text{-Ha}} = {}^3J_{5,6\text{-Hb}} = 6.8$ Hz, 1 H, 5b-H), 4.13 (m, 3 H, 6b-H_a, 6b-H_b, 5c-H), 4.32 (dd, $^2J_{6\text{-Hb},6\text{-Ha}} = 10.6$, $^3J_{6\text{-Hb},5} = 4.9$ Hz, 1 H, 6a-H_b), 4.52 (d, $^3J_{1,2} = 7.4$ Hz, 1 H, 1a-H), 4.89 (d, $^3J_{1,2} = 7.8$ Hz, 1 H, 1b-H), 4.94 (dd, $^3J_{4,3} = {}^3J_{4,5} = 10.1$ Hz, 1 H, 4c-H), 5.09 (d, $^3J_{1,2} = 2.3$ Hz, 1 H, 1c-H), 5.10 (dd, $^3J_{2,1} = 7.8$, $^3J_{2,3} = 10.3$ Hz, 1 H, 2b-H), 5.17 (dd, $^3J_{3,2} = 10.4$, $^3J_{3,4} = 3.4$ Hz, 1 H, 3b-H), 5.24 (dd, $^3J_{3,2} = 3.6$, $^3J_{3,4} = 10.2$ Hz, 1 H, 3c-H), 5.30 (dd, $^3J_{2,1} = 2.3$, $^3J_{2,3} = 3.6$ Hz, 1 H, 2c-H), 5.37 (dd, $^3J_{4,3} = 3.4$, $^3J_{4,5} < 1$ Hz, 1 H, 4b-H), 7.32 (m, 3 H, Ph), 7.46 (m, 2 H, Ph). ^{13}C NMR (151 MHz, $CDCl_3$, selected data, ppm): δ = 12.0 (18′-, 19′-C), 16.6 (6c-C), 18.6 (21′-C), 20.5–20.7 (7 OCO*C*H_3), 22.5 (26′-C), 22.7 (27′-C), 60.9 (6b-C), 65.9 (5a-C), 66.3 (5c-C), 67.2 (4b-C), 68.7 (6a-C), 68.9 (3c-C), 69.6 (2c-C), 70.2 (2b-C), 70.6 (3b-, 5b-C), 70.7 (4c-C), 77.2 (3a-C), 78.7 (4a-C), 79.9 (3′-C), 80.5 (2a-C), 97.4 (1c-C), 99.5 (1b-C), 100.8 (1a-C), 101.7 (PhCH), 126.3 (2 Ph-C), 128.0 (2 Ph-C), 129.0 (1 Ph-C), 137.1 (1 Ph-C), 169.3–170.3 (7 O*C*OCH$_3$). $C_{66}H_{96}O_{22}$ (1241.4). MALDI-MS (positive Mode, Matrix DHB, THF): 1279.1 [M + K]$^+$.

3β-*O*-{2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→2)-[2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)]-6-deoxy-β-D-glucuronopyranosyl}cholestanol (46): The trisaccharide saponin **45** (110 mg, 0.089 mmol) was dissolved in CH_2Cl_2 (2 mL). The solution was treated with ethanthiol (50 μL) and acidified with *p*-toluenesulfonic acid. After stirring for 1 h the benzylidene deprotection was completed (R_f = 0.22, PE/EtOAc, 1:1). The reaction was quenched with NEt_3 and concentrated. The residue was passed through a short silica gel column (PE/EtOAc, 1:1) to give the debenzylidenated saponin (90 mg, 0.078 mmol, 88%), which was directly subjected to oxidation. The said debenzylidenated saponin (60 mg, 0.052 mmol) was dissolved in dichloromethane/saturated $NaHCO_3$ solution/water (10:1:1, 4 mL). Tetrabutylammonium chloride (100 μL, 6.5% solution), potassium bromide (100 μL, 10% solution) and TEMPO (90 μL, 3% solution in CH_2Cl_2) were added. The reaction was activated by dropping fresh sodium hypochlorite solution (100 μL, 13% chlorine) to the well stirred mixture. TLC control showed formation of the glucuronic acid (toluene/acetone, 1:3) and disappearance of the starting material. The reaction was diluted with dichloromethane and washed with saturated Na_2SO_3 solution. The organic layer was separated and concentrated. Purification by flash chromatography (SiO_2, 2×7, toluene/acetone, 1:1 → 1:2 acidified by TFA) afforded the glucuronic acid saponin **46** (45 mg, 0.038 mmol, 73%). R_f(product) = 0.42 (toluene/acetone, 1:3). ^{1}H NMR (250 MHz, $CDCl_3$ + 1 drop CD_3OD, ppm): δ = 0.61 (s, 3 H, 18′-CH_3), 0.78 (s, 3 H, 19′-CH_3), 0.83–0.88 (m, 12 H, 6c-, 21′-, 26′-, 27′-CH_3), 1.07–2.14 (m, 52 H, 7 H_3CCO), 3.59–4.11 (m, 9 H, 2a-, 3a-, 4a-, 5a-H, 3′-H, 5b-H, 6b-H_a, 6b-H_b, 5c-H), 4.58 (br. s, 1 H, 1a-H), 4.88 (d, $^3J_{1,2} = 7.7$ Hz, 1 H, 1b-H), 5.03–5.31 (m, 6 H, 1c-, 2c-, 3c-, 4c-, 2b-, 3b-H), 5.38 (dd, $^3J_{4,3} = 1$, $^3J_{4,5} < 1$ Hz, 1 H, 4b-H). $C_{59}H_{90}O_{23}$ (1167.3). MALDI-MS (positive Mode, Matrix DHB, THF): 1189.6 [M + Na]$^+$. FAB-MS (positive Mode, Matrix NBA, THF): 1211 [(M + Na – H)Na]$^+$.

3β-*O*-{β-D-Galactopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→3)]-6-deoxy-β-D-glucuronopyranosyl}cholestanol (47): A solution of the acetylated saponin **46** (7 mg, 6.0 μmol) in dichloromethane/methanol (1:2, 3 mL) was treated with sodium methoxide (1 mg). Neutralization with ion exchange resin IR-120 (H$^+$), filtration and evaporation gave the pure deprotected neosaponin **47** (5 mg, 5.7 μmol, 95%). R_f(product) = 0.52 (chloroform/methanol/water, 60:35:7). ^{1}H NMR (250 MHz, $CDCl_3$/MeOD/D_2O, 65:35:3, ppm): δ = 0.38 (s, 3 H, 18′-CH_3), 0.54 (s, 3 H, 19′-CH_3), 0.58–0.64 (m, 12 H, 6c-, 21′-, 26′-, 27′-CH_3), 3.05–3.71 (m, 14 H, 2a-, 3a-, 4a-, 5a-H, 3′-H, 2b-, 3b-, 5b-H, 6b-H_a, 6b-H_b, 2c-, 3c-, 4c-, 5c-H), 3.80 (dd, $^3J_{4,3} = 1$, $^3J_{4,5} < 1$ Hz, 1 H, 4b-H), 4.31–4.38 (m, 2 H, 1a-, 1b-H), 4.82 (d, dd, $^3J_{1,2} = 1$ Hz, 1 H, 1c-H). $C_{45}H_{76}O_{16}$ (873.0). MALDI-MS (positive Mode, Matrix DHB, MeOH): 894.8 [M + Na]$^+$, 911.7 [M + K]$^+$, 933.2 [(M – H + Na)K]$^+$.

3β-*O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)friedelanol (48): To a solution of β-*O*-friedelanol (470 mg, 1.10 mmol) and trichloroacetimidate **19** (837 g, 1.32 mmol), in dry CH_2Cl_2 (22 mL) stirred under nitrogen at room temp. was added dropwise TMSOTf (0.05 M solution in CH_2Cl_2, 14 μL, 0.08 mmol). After 30 min the reaction mixture was neutralized with triethylamine evaporated and purified by flash chromatography (petroleum ether/ethyl acetate, 10:1) to afford **48** (537 mg, 54%) and 2-*O*-acetylfriedelanol (103.6 mg, 20%). TLC (petroleum ether/ethyl acetate, 8:1): R_f = 0.38. $[\alpha]_D$ = +16.2 (c = 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.83–0.84 (m, 10 H, 25′-CH_3, 24′-CH_3, 23′-CH_3, 10′-H), 0.91–0.94 (m, 6 H, 6′-H_a, 16′-H_a, 22′-H_a, 30′-CH_3), 0.98–1.00 (m, 9 H, 26′-CH_3, 27′-CH_3, 29′-CH_3), 1.10–1.15 (m, 1 H, 1′-H_a), 1.17 (s, 3 H, 28′-CH_3), 1.18–1.59 (m, 18 H, 19′-H_a, 11′-H_a, 4′-H, 15′-H_a, 21′-H_a, 12′-$H_{a,b}$, 19′-H_b, 11′-H_b, 7′-H_a, 2′-H_a, 15′-H_b, 21′-H_b, 16′-H_b, 22′-H_b, 18′-H, 1′-H_b, 7′-H_b), 1.69 (br. d, 1 H, 6′-H_b), 1.96 (s, 3 H, Ac), 2.20 (br. d, 1 H, 2′-H_b), 3.44 (br. s, 1 H, 5-H), 3.52 (br. s, 1 H, 3′-H), 3.62–3.67 (m, 3 H, 3-H, 4-H, 6-H_a), 3.72 (dd, $J_{gem} = 10.8$, $J_{6,5} < 1.0$ Hz, 1 H, 6-H_b), 4.30 (d, $J_{1,2} = 7.9$ Hz, 1 H, 1-H), 4.58 (2d, $J_{gem} = 11.2$ Hz, 2 H, 2 CH_2Ph), 4.62 (d, $J_{gem} = 12.4$ Hz, 1 H, CH_2Ph), 4.67 (d, $J_{gem} = 11.5$ Hz, 1 H, CH_2Ph), 4.79 (2d, $J_{gem} = 11.5$ Hz, 2 H, 2 CH_2Ph), 5.03 (dd, $J_{2,1} = J_{2,3} = 7.9$ Hz, 1 H, 2-H), 7.21–7.33 (m, 15 H, 3 Ph). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 11.5 (1 C, 23′-C), 16.0 (1 C, 25′-C), 16.5 (1 C, 7′-C), 18.3 (1 C, 24′-C), 18.6 (1 C, 27′-C), 20.1 (1 C, 26′-C), 21.0 (1 C, *C*H_3CO), 30.6 (1 C, 12′-C), 31.8 (1 C, 29′-C), 32.1 (1 C, 28′-C), 32.3 (2 C, 15′-C, 21′-C), 34.2 (1 C, 2′-C), 35.0 (1 C, 30′-C), 35.3 (2 C, 19′-C, 11′-C), 35.6 (1 C, 1′-C), 39.3 (2 C, 16′-C, 22′-C), 41.8 (1 C, 6′-C), 35.3 (1 C, 18′-C), 49.4 (1 C, 4′-C), 53.2 (1 C, 8′-C), 61.4 (1 C, 10′-C), 68.9 (1 C, 6-H), 73.4 (1 C, 2′-C), 73.5 (1 C, *C*H_2Ph), 75.0 (3 C, 2 *C*H_2Ph, 5-C), 78.2 (1 C, 4-C), 83.1 (1 C, 3-

C), 83.2 (1 C, 3-C), 103.1 (1 C, 1-C), 127.5, 127.6, 127.8, 128.0, 128.3, 128.4 (15 C, 3 Ph), 137.97, 138.3 (3 C, *ipso*-Ph), 169.2 (1 C, CH_3CO). MALDI-MS (positive mode, matrix DHB, THF): *m/z* = 926 [*M* + Na]$^+$, 943 [*M* + K]$^+$. $C_{59}H_{82}O_7$ (903.3): calcd. C 78.45, H 9.15; found C 78.49, H 9.45.

3β-*O*-(3,4,6-Tri-*O*-benzyl-β-D-glucopyranosyl)friedelanol (49β): A solution of compound **48** (537 mg, 0.60 mmol) in a mixture of dry CH_3OH/CH_2Cl_2 (2.3:1, 100 mL) was treated with sodium methoxide (1 N solution in CH_3OH, 1 mL) and stirred at room temp. After 24 h the solution was neutralized with ion-exchange resin (Amberlite IR-120 H^+), the resin was filtered off and the filtrate concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 10:1) to afford **49β** (434 mg, 84%). TLC (petroleum ether/ethyl acetate, 8:1): R_f = 0.33. $[\alpha]_D$ = +5.7 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.86 (s, 3 H, 24′-CH_3), 0.88–0.95 (m, 13 H, 10′-H, 16′-H_a, 22′-H_a, 23′-CH_3, 25′-CH_3, 30′-CH_3, 6′-H_a), 1.00–1.01 (3s, 9 H, 26′-CH_3, 29′-CH_3, 27′-CH_3), 1.11–1.16 (m, 1 H, 1′-H_a), 1.18–1.22 (m, 5 H, 28′-CH_3, 19′-H_a, 11′-H_a), 1.26–1.60 (m, 17 H, 15′-H_a, 21′-H_a, 8′-H, 4′-H, 12′-$H_{a,b}$, 19′-H_b, 11′-H_b, 7′-H_a, 15′-H_b, 21′-H_b, 2′-H_a, 16′-H_b, 22′-H_b, 1′-H_b, 18′-H, 7′-H_b), 1.73 (br. d, 1 H, 6′-H_b), 2.22 (br. d, 1 H, 2′-H_b), 3.45–3.47 (m, 1 H, 5-H), 3.53–3.61 [m, 3 H, H,H-COSY: 3.55 (4-H), 3.58 (2-H), 3.59 (3-H)], 3.63–3.66 (m, 2 H, 3′-H, 6-H_a), 3.72 (dd, J_{gem} = 10.5, $J_{6,5}$ < 1.0 Hz, 1 H, 6-H_b), 4.22 (d, $J_{1,2}$ = 7.0 Hz, 1 H, 1-H), 4.56 (d, J_{gem} = 10.9 Hz, 1 H, CH_2Ph), 4.57 (d, J_{gem} = 12.3 Hz, 1 H, CH_2Ph), 4.61 (d, J_{gem} = 12.4 Hz, 1 H, CH_2Ph), 4.81 (d, J_{gem} = 11.2 Hz, 1 H, CH_2Ph), 4.85 (d, *J* = 10.9 Hz, 1 H, CH_2Ph), 4.98 (d, *J* = 11.2 Hz, 1 H, CH_2Ph), 7.20–7.38 (m, 15 H, 3 Ph). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 11.9 (1 C, 23′-C), 16.3 (1 C, 25′-C), 16.5 (1 C, 7′-C), 18.3 (1 C, 24′-C), 18.6 (1 C, 27′-C), 20.1 (1 C, 26′-C), 30.6 (1 C, 12′-C), 31.8 (1 C, 29′-C), 32.1 (1 C, 28′-C), 32.8 (2 C, 15′-C, 21′-C), 34.3 (1 C, 2′-C), 35.0 (1 C, 30′-C), 35.3 (2 C, 19′-C, 21′-C), 35.6 (1 C, 1′-C), 39.3 (2 C, 16′-C, 22′-C), 41.6 (1 C, 6′-C), 42.8 (1 C, 18′-C), 49.4 (1 C, 4′-C), 53.2 (1 C, 8′-C), 61.4 (1 C, 10′-C), 69.1 (1 C, 6-C), 73.4 (1 C, *C*H_2Ph), 75.1 (3 C, 2 *C*H_2Ph, 5-C), 75.8 (1 C, 2-C), 77.6 (1 C, 4-C), 83.1 (1 C, 3′-C), 84.6 (1 C, 3-C), 105.0 (1 C, 1-C), 127.5, 127.6, 127.7, 127.9, 128.0, 128.4 (15 C, 3 Ph), 138.2, 138.4, 138.8 (3 C, *ipso*-Ph). MALDI-MS (positive mode, matrix DHB, THF): *m/z* = 884 [*M* + Na]$^+$, 900 [*M* + K]$^+$. $C_{57}H_{80}O_6$ (861.3): calcd. C 79.49, H 9.36; found C 78.83, H 9.47.

3β-*O*-(3,4,6-Tri-*O*-benzyl-α-D-glucopyranosyl)friedelanol (49α) and 3β-*O*-[(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)-(3,4,6-*O*-benzyl-α-D-glucopyranosyl)]friedelanol (50α): TMSOTf (0.03 M solution in CH_2Cl_2, 0.5 μL, 2.8 μmol) was added to a solution of **49β** (35 mg, 0.04 mmol) in dry CH_2Cl_2 (4 mL) and stirred under nitrogen at room temp. A solution of trichloroacetimidate **13** (39 mg, 0.08 mmol) in dry CH_2Cl_2 (1 mL) was added dropwise. After stirring for 30 min reaction mixture was neutralized with triethylamine, concentrated in vacuo and purified by flash chromatography (petroleum ether/ethyl acetate, 5:1) to afford **49α** (6 mg, 12%) and **50α** (12 mg, 25%). **49α**: TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.53. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.86 (2s, 6 H, 24′-CH_3, 25′-CH_3), 0.89–0.96 (m, 9 H, 10′-H, 23′-CH_3, 16′-H_a, 22′-H_a, 30′-CH_3), 1.12–1.13 (m, 10 H, 6′-H_a, 29′-CH_3, 26′-CH_3, 27′-CH_3), 1.19–1.75 (m, 24 H, 1′-H_a, 28′-CH_3, 2′-H_a, 19′-H_a, 11′-H_a, 15′-H_a, 21′-H_a, 8′-H, 7′-H_a, 4′-H, 12′-$H_{a,b}$, 19′-H_b, 11′-H_b, 7′-H_b, 16′-H_b, 22′-H_b, 15′-H_b, 21′-H_b, 18′-H, 1′-H_b, 6′-H_b), 2.01 (br. d, 1 H, 2′-H_b), 3.62–3.65 [m, 3 H, H,H-COSY: 3.62 (3-H, 4-H), 3.64 (6-H_a)], 3.70–3.72 (m, 2 H, 2-H, 3′-H), 3.76 (dd, $J_{6,5}$ = 3.6, J_{gem} = 10.6 Hz, 1 H, 6-H_b), 3.90 (br. d, 1 H, 5-H), 4.51 (d, J_{gem} = 12.0 Hz, 1 H, CH_2Ph), 4.52 (d, 1 H, CH_2Ph), 4.64 (d, J_{gem} = 12.2 Hz, 1 H, CH_2Ph), 4.85 (d, J_{gem} = 11.0 Hz, 1 H, CH_2Ph), 4.86 (d, J_{gem} = 11.0 Hz, 1 H, CH_2Ph), 4.89 (d, $J_{1,2}$ = 4.0 Hz, 1 H, 1-H), 4.94 (d, J_{gem} = 11.3 Hz, 1 H, CH_2Ph), 7.18–7.42 (m, 15 H, 3 Ph). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 13.0 (1 C, 23′-C), 16.5 (1 C, 7′-C), 17.1 (1 C, 25′-C), 18.8 (1 C, 24′-C), 19.1 (1 C, 27′-C), 20.6 (1 C, 26′-C), 29.7 (2 C, 2′-C, 12′-C), 32.0 (1 C, 29′-C), 32.2 (1 C, 28′-C), 32.6 (2 C, 15′-C, 21′-C), 35.3 (3 C, 30′-C, 19′-C, 21′-C), 35.9 (1 C, 1′-C), 39.7 (2 C, 16′-C, 22′-C), 42.2 (1 C, 6′-C), 43.1 (1 C, 18′-C), 49.0 (1 C, 4′-C), 53.5 (1 C, 8′-C), 61.9 (1 C, 10′-C), 68.8 (1 C, 6-C), 71.4 (1 C, 5-C), 73.1 (1 C, 2-C), 73.9 (1 C, *C*H_2Ph), 75.5 (2 C, *C*H_2Ph), 77.6 (C, 4-C), 77.8 (1 C, 3′-C), 83.6 (1 C, 3-C), 96.1 (1 C, 1-C). MALDI-MS (positive mode, matrix DHB, THF): *m/z* = 885 [*M* + Na]$^+$, 902 [*M* + K]$^+$. $C_{57}H_{80}O_6$ (861.3).

50α: TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.38. $[\alpha]_D$ = +4.1 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.90–0.91 (m, 6 H, 10′-H, 23′-CH_3, 16′-H_a, 22′-H_a), 0.95–0.97 (m, 10 H, 30′-CH_3, 6′-H_a, 25′-CH_3, 24′-CH_3), 1.00 (s, 6 H, 26′-CH_3, 29′-CH_3), 1.01 (s, 3 H, 27′-CH_3), 1.12–1.56 (m, 20 H, 1′-H_a, 28′-CH_3, 19′-H_a, 11′-H_a, 15′-H_a, 21′-H_a, 8′-H, 12′-$H_{a,b}$, 2′-H_a, 4′-H, 19′-H_b, 11′-H_b, 7′-H_a, 15′-H_b, 21′-H_b, 18′-H, 1′-H_b), 1.68–1.75 (m, 5 H, 6′-H_b, 7′-H_b, Ac), 1.98, 2.05 (2s, 6 H, 2 Ac), 2.14–2.18 (m, 4 H, Ac, 2′-H_b), 3.59–3.62 [m, 3 H, H,H-COSY: 3.60 (6a-H_a), 3.61 (4a-H), 3.62 (3′-H)], 3.70–3.74 (m, 2 H, 2a-H, 6a-H_b), 3.85 (dd, $J_{3,2}$ = $J_{3,4}$ = 9.4 Hz, 1 H, 3a-H), 3.89–3.93 (m, 2 H, 5b-H, 5a-H), 4.06–4.15 (m, 2 H, 6b-$H_{a,b}$), 4.45 (2d, 2 H, 2 CH_2Ph), 4.59 (d, J_{gem} = 12.1 Hz, 1 H, CH_2Ph), 4.70 (d, J_{gem} = 11.4 Hz, 1 H, CH_2Ph), 4.72 (d, J_{gem} = 11.4 Hz, 1 H, CH_2Ph), 4.77 (d, *J* = 10.8 Hz, 1 H, CH_2Ph), 4.85 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1b-H), 4.99 (d, $J_{1,2}$ = 4.0 Hz, 1 H, 1a-H), 4.99–5.01 (m, 1 H, 3b-H), 5.25 (dd, $J_{2,3}$ = 10.3, $J_{2,1}$ = 8.0 Hz, 1 H, 2b-H), 5.37 (d, *J* = 2.6 Hz, 1 H, 4b-H), 7.10–7.34 (m, 15 H, 3 Ph). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 12.7 (1 C, 23′-C), 16.1, 16.2 (2 C, 7′-C, 25′-C), 18.1 (1 C, 24′-C), 18.7 (1 C, 27′-C), 20.1, 29.6, 20.7 (5 C, 26′-C, 4 *C*H_3CO), 30.7 (2 C, 2′-C, 12′-C), 31.8 (1 C, 29′-C), 32.1 (1 C, 28′-C), 32.8 (2 C, 15′-C, 21′-C), 35.0, 35.3 (3 C, 30′-C, 19′-C, 21′-C), 36.0 (1 C, 1′-C), 39.3 (2 C, 16′-C, 22′-C), 42.0 (1 C, 6′-C), 42.8 (1 C, 18′-C), 49.1 (1 C, 4′-C), 53.2 (1 C, 8′-C), 61.2 (1 C, 6b-C), 61.8 (1 C, 10′-C), 67.3 (1 C, 4b-C), 68.6 (1 C, 6a-C), 69.0 (1 C, 2b-C), 70.4 (1 C, 5a-C), 70.7 (1 C, 5b-C), 71.2 (1 C, 3b-C), 73.5, 75.0 (3 C, 3 *C*H_2Ph), 77.9 (1 C, 3′-C), 78.0 (1 C, 4a-C), 80.0 (1 C, 2a-C), 81.3 (1 C, 3a-C), 95.9 (1 C, 1a-C), 101.9 (1 C, 1b-C), 127.6, 127.7, 127.9, 128.3, 128.5 (15 C, 3 Ph), 138.0 (3 C, *ipso*-Ph), 168.8, 170.2 (4 C, 4 CH_3CO). MALDI-MS (positive mode, matrix DHB, THF): *m/z* = 1215 [*M* + Na]$^+$. $C_{71}H_{98}O_{15}$ (1191.5): calcd. C 71.57, H 8.29; found C 71.11, H 8.37.

3β-*O*-[(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)-(3,4,6-*O*-benzyl-β-D-glucopyranosyl)]friedelanol (50β): To a solution of **49β** (286 mg, 0.33 mmol) and **13** (328 mg, 0.66 mmol) in dry CH_2Cl_2 (7 mL) was added TMSOTf (0.03 M solution in CH_2Cl_2, 4 μL, 22.1 μmol) and the reaction mixture was stirred under nitrogen at room temp. After stirring for 15 min the reaction mixture was neutralized with triethylamine, concentrated in vacuo and purified by flash chromatography (petroleum ether/ethyl acetate, 5:1) to afford **50β** (311 mg, 78%). TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.38. $[\alpha]_D$ = –3.6 (*c* = 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.85–0.87 (m, 4 H, 10′-H, 24′-CH_3), 0.90–0.94 (m, 5 H, 16′-H_a, 22′-H_a, 30′-CH_3), 0.98–1.03 (m, 13 H, 6′-H_a, 25′-CH_3, 26′-CH_3, 29′-CH_3, 27′-CH_3), 1.03 (d $J_{23,4}$ = 6.9 Hz, 3 H,, 23′-CH_3), 1.10–1.59 (m, 22 H, 1′-H_a, 28′-CH_3, 19′-H_a, 11′-H_a, 4′-H, 15′-H_a, 21′-H_a, 8′-H, 12′-$H_{a,b}$, 19′-H_b, 11′-H_b, 7′-H_a, 2′-H_a, 15′-H_b, 21′-H_b, 16′-H_b, 22′-H_b, 18′-H, 7′-H_b, 1′-H_b), 1.73 (br. d, 1 H, 6′-H_b), 1.98, 2.03, 2.06, 2.15 (4s, 12 H, 4 Ac), 2.22 (br. d, 1 H, 2′-H_b), 3.40 (br. s, 1 H, 5a-H), 3.52 (br. s, 1 H, 3′-H), 3.57–3.59 (m, 2 H, 3a-H, 4a-H), 3.64 (dd, $J_{6,5}$ = 4.7, J_{gem} = 10.8 Hz, 1 H, 6a-H_a), 3.69 (br. s, 1

H, 6a-H_b), 3.74 (dd, $J_{5,6\text{-Ha}} = J_{5,6\text{-Hb}} = 6.6$ Hz, 1 H, 5b-H), 3.84 (dd, $J_{2,3} = J_{2,1} = 8.0$ Hz, 1 H, 2a-H), 4.05–4.13 (m, 2 H, 6b-$H_{a,b}$), 4.20 (d, $J_{1,2} = 7.7$ Hz, 1 H, 1a-H), 4.57 (d, $J_{gem} = 12.3$ Hz, 1 H, CH_2Ph), 4.61 (2d, 2 H, 2 CH_2Ph), 4.73 (d, $J_{gem} = 10.1$ Hz, 1 H, CH_2Ph), 4.79 (d, $J_{gem} = 11.0$ Hz, 1 H, CH_2Ph), 4.88 (d, $J = 10.1$ Hz, 1 H, CH_2Ph), 4.91 (dd, $J_{3,2} = 10.4$, $J_{3,4} = 3.1$ Hz, 1 H, 3b-H), 5.05 (d, $J_{1,2} = 8.0$ Hz, 1 H, 1b-H), 5.20 (dd, $J_{2,1} = 8.2$, $J_{2,3} = 10.1$ Hz, 1 H, 2b-H), 5.32 (d, $J_{4,3} = 2.7$ Hz, 1 H, 4b-H), 7.20–7.38 (m, 15 H, 3 Ph). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): $\delta = 11.5$ (1 C, 23′-C), 16.7 (2 C, 7′-C, 25′-C), 18.3 (1 C, 24′-C), 18.6 (1 C, 27′-C), 20.1 (1 C, 26′-C), 20.6, 20.7 (4 C, 4 *C*H_3CO), 30.6 (1 C, 12′-C), 31.8 (1 C, 29′-C), 32.1 (1 C, 28′-C), 32.3 (2 C, 15′-C, 21′-C), 34.5 (1 C, 2′-C), 35.0 (1 C, 30′-C), 35.3 (2 C, 19′-C, 21′-C), 35.6 (1 C, 1′-C), 39.3 (2 C, 16′-C, 22′-C), 42.0 (1 C, 6′-C), 42.8 (1 C, 18′-C), 49.9 (1 C, 4′-C), 53.2 (1 C, 8′-C), 61.0 (1 C, 6b-C), 61.4 (1 C, 10′-C), 67.3 (1 C, 4b-C), 68.8 (1 C, 6a-C), 69.7 (1 C, 2b-C), 70.4 (1 C, 5b-C), 71.2 (1 C, 3b-C), 73.4 (1 C, *C*H_2Ph), 74.8 (2 C, *C*H_2Ph, 5a-C), 75.6 (1 C, *C*H_2Ph), 76.2 (1 C, 2a-C), 78.5 (1 C, 4a-C), 84.1 (1 C, 3′-C), 86.4 (1 C, 3a-C), 99.7 (1 C, 1b-C), 104.4 (1 C, 1a-C), 127.5, 127.6, 127.8, 128.0, 128.1, 128.3, 128.4, 128.7 (15 C, 3 Ph), 137.8, 137.9, 138.2 (3 C, *ipso*-Ph), 169.1, 170.2, 170.4 (4 C, 4 CH_3*C*O). MALDI-MS (positive mode, matrix DHB, THF): *m*/*z* = 1215 $[M + Na]^+$. $C_{71}H_{98}O_{15}$ (1191.5): calcd. C 71.57, H 8.29; found C 71.05, H 8.68.

3β-*O*-[(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)-(β-D-glucopyranosyl)]friedelanol (51): Palladium on carbon (311 mg, 10% Pd) was added to compound **50β** (311 mg, 0.26 mmol) dissolved in a mixture CH_3OH/CH_2Cl_2 (2.2:1, 22 mL) and the suspension was vigorously stirred under hydrogen atmosphere at room temp. After 30 min the mixture was filtered and the filtrate concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:3) to afford **51** (228 mg, 95%) which was immediately used in the next step. TLC (ethyl acetate): $R_f = 0.25$. MALDI-MS (positive mode, matrix DHB, THF): *m*/*z* = 945 $[M + Na]^+$, 961 $[M + K]^+$. $C_{50}H_{80}O_{15}$ (921.2).

3β-*O*-[(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)-(3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)]friedelanol (52): To a solution of **51** (92 mg, 0.10 mmol) in dry acetonitrile (7 mL) were added benzaldehyde dimethyl acetal (18 μL, 0.12 mmol) and *p*-toluenesulfonic acid (1 mg, 5 μmol). The reaction mixture was stirred for 15 min, quenched with triethylamine and the solvents evaporated. Purification by flash chromatography (petroleum ether/ethyl acetate, 3:1) afforded **52** (92 mg, 92%). TLC (petroleum ether/ethyl acetate, 1:2): $R_f = 0.68$. $[\alpha]_D = -1.0$ ($c = 0.2$, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): $\delta = 0.85$–0.87 (m, 4 H, 10′-H, 24′-CH_3), 0.90–0.94 (m, 5 H, 16′-H_a, 22′-H_a, 30′-CH_3), 0.96–0.97 (m, 4 H, 6′-H_a, 25′-CH_3), 0.96 (s, 3 H, 26′-CH_3) 0.99, 1.00 (2s, 6 H, 29′-CH_3, 27′-CH_3) 1.02 (d $J_{23,4} = 7.0$ Hz, 3 H,, 23′-CH_3), 1.07–1.56 (m, 23 H, 1′-H_a, 19′-H_a, 11′-H_a, 28′-CH_3, 4′-H, 15′-H_a, 21′-H_a, 8′-H, 12′-$H_{a,b}$, 19′-H_b, 11′-H_b, 7′-H_a, 2′-H_a, 15′-H_b, 21′-H_b, 16′-H_b, 22′-H_b, 18′-H, 1′-H_b, 7′-H_b), 1.72 (br. d, 1 H, 6′-H_b), 1.98 (s, 3 H, Ac), 2.05–2.11 (m, 7 H, 2 Ac, 2′-H_b), 2.15 (s, 3 H, Ac), 3.35 (ddd, $J_{5,6\text{-Ha}} = 5.0$, $J_{5,6\text{-Hb}} = J_{5,4} = 9.6$ Hz, 1 H, 5a-H), 3.51–3.54 (m, 1 H, 4a-H), 3.56 (br. s, 1 H, 3′-H), 3.75 (dd, $J_{gem} = J_{6,5} = 10.3$ Hz, 1 H, 6a-H_a), 3.80–3.81 (m, 2 H, 2a-H, 3a-H), 3.89 (dd, $J_{5,4} = J_{5,6} = 6.7$ Hz, 1 H, 5b-H), 4.12–4.15 (m, 2 H, 6b-$H_{a,b}$), 4.30 (dd, $J_{6,5} = 5.0$, $J_{gem} = 10.5$ Hz, 1 H, 6a-H_b), 4.36 (d, $J_{1,2} = 6.7$ Hz, 1 H, 1a-H), 5.02 (dd, $J_{3,2} = 10.3$, $J_{3,4} = 3.2$ Hz, 1 H, 3b-H), 5.11 (dd, $J_{1,2} = 7.9$ Hz, 1 H, 1b-H), 5.16 (dd, $J_{2,1} = 8.0$, $J_{2,3} = 10.1$ Hz, 1 H, 2b-H), 5.36 (d, $J_{4,3} = 3.0$ Hz, 1 H, 4b-H), 5.51 (s, 1 H, C*H*Ph), 7.26–7.49 (m, 5 H, Ph). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): $\delta = 11.5$ (1 C, 23′-C), 16.4 (1 C, 25′-C), 16.6 (1 C, 7′-C), 18.3 (1 C, 24′-C), 18.6 (1 C, 27′-C), 20.1 (1 C, 26′-C), 20.6, 20.7, 20.9 (4 C, 4 *C*H_3CO), 30.0 (1 C, 12′-C), 31.8 (1 C, 29′-C), 32.1 (1 C, 28′-C), 32.4 (2 C, 15′-C, 21′-C), 34.5 (1 C, 2′-C), 35.0 (1 C, 30′-C), 35.4 (2 C, 19′-C, 21′-C), 35.6 (1 C, 1′-C), 39.7 (2 C, 16′-C, 22′-C), 42.0 (1 C, 6′-C), 42.9 (1 C, 18′-C), 49.9 (1 C, 4′-C), 53.3 (1 C, 8′-C), 61.5 (1 C, 6b-C), 61.8 (1 C, 10′-C), 65.9 (1 C, 5a-C), 67.5 (1 C, 4b-C), 69.1 (1 C, 6a-C), 70.1 (1 C, 2b-C), 70.7 (1 C, 5b-C), 71.4 (1 C, 3b-C), 75.6 (1 C, 2a-C), 78.4 (1 C, 3a-C), 80.9 (1 C, 4a-C), 84.8 (1 C, 3′-C), 100.4 (1 C, 1b-C), 102.2 (1 C, *C*HPh), 104.9 (1 C, 1a-C), 126.7, 128.7 (5 C, Ph), 137.2 (1 C, *ipso*-Ph), 169.0–170.4 (4 C, 4 CH_3*C*O). MALDI-MS: *m*/*z* = 1032 $[M + Na]^+$, 1048 $[M + K]^+$. $C_{57}H_{84}O_{15}$ (1009.3): calcd. C 67.83, H 8.39; found C 67.37, H 9.00.

3β-*O*-{(2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)]-(4,6-*O*-benzylidene-β-D-glucopyranosyl)}friedelanol (53): Compound **52** (92 mg, 0.09 mmol) and **16** (77 mg, 0.18 mmol) in dry CH_2Cl_2 (2 mL) were stirred under nitrogen at room temp. for 5 min. TMSOTf (0.06 M solution in CH_2Cl_2, 1 μL, 5.5 μmol) was added dropwise and the reaction mixture was stirred for 15 min. The reaction mixture was neutralized with triethylamine, concentrated in vacuo and purified by flash chromatography (petroleum ether/ethyl acetate, 2:1 → 1:1) to afford **53** (109 mg, 94%). TLC (petroleum ether/ethyl acetate, 2:1): $R_f = 0.68$. $[\alpha]_D = -1.5$ ($c = 0.1$, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): $\delta = 0.85$–0.87 (m, 4 H, 10′-H, 24′-CH_3), 0.90–0.94 (m, 5 H, 16′-H_a, 22′-H_a, 30′-CH_3), 0.96–0.97 (m, 4 H, 6′-H_a, 25′-CH_3), 0.98 (s, 3 H, 26′-CH_3), 0.99 (2s, 6 H, 29′-CH_3, 27′-CH_3), 1.02 (d $J_{23,4} = 7.0$ Hz, 3 H,, 23′-CH_3), 1.07–1.56 (m, 23 H, 1′-H_a, 28′-CH_3, 19′-H_a, 11′-H_a, 4′-H, 15′-H_a, 21′-H_a, 8′-H, 12′-$H_{a,b}$, 19′-H_b, 11′-H_b, 7′-H_a, 2′-H_a, 15′-H_b, 21′-H_b, 16′-H_b, 22′-H_b, 7′-H_b, 18′-H, 1′-H_b), 1.72 (br. d, 1 H, 6′-H_b), 1.96, 2.00, 2.01, 2.04, 2.07 (5s, 15 H, 5 Ac), 2.08–2.09 (m, 4 H, 2′-H_b, Ac), 2.15 (s, 3 H, Ac), 3.06 (dd, $J_{5,4} = 7.0$, $J_{gem} = 12.2$ Hz, 1 H, 5c-H_a), 3.37 (ddd $J_{5,6\text{-Ha}} = 4.9$, $J_{5,6\text{-Hb}} = J_{5,4} = 9.5$ Hz, 1 H,, 5a-H), 3.51 (br. s, 1 H, 3′-H), 3.72–3.77 (m, 2 H, 4b-H, 6a-H_a), 3.94–3.96 [m, 3 H, H,H-COSY: 3.94 (5b-H), 3.95 (2a-H), 3.96 (3a-H)], 4.10–4.16 (m, 3 H, 5c-H, 6b-$H_{a,b}$), 4.28 (dd, $J_{6,5} = 5.0$, $J_{gem} = 10.6$ Hz, 1 H, 6a-H_b), 4.31 (d, $J_{1,2} = 6.8$ Hz, 1 H, 1a-H), 4.81 (dd, 1 H, 4c-H), 4.89 (d, $J_{1,2} = 4.5$ Hz, 1 H, 1c-H), 4.93 (d, $J_{1,2} = 7.9$ Hz, 1 H, 1b-H), 4.93–5.00 (m, 1 H, 2c-H, 3c-H), 5.11 (dd, $J_{2,1} = 8.0$, $J_{2,3} = 10.0$ Hz, 1 H, 2b-H), 5.25 (dd, $J_{3,4} = 3.5$, $J_{3,2} = 10.4$ Hz, 1 H, 3b-H), 5.36 (d, $J_{4,3} = 3.0$ Hz, 1 H, 4b-H), 5.46 (s, 1 H, C*H*Ph), 7.26–7.45 (m, 5 H, Ph). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): $\delta = 11.6$ (1 C, 23′-C), 16.6 (1 C, 25′-C), 17.2 (1 C, 7′-C), 19.0 (1 C, 24′-C), 19.2 (1 C, 27′-C), 20.4 (1 C, 26′-C), 20.7, 20.9 (7 C, 7 *C*H_3CO), 31.0 (1 C, 12′-C), 31.8 (1 C, 29′-C), 32.1 (1 C, 28′-C), 32.4 (2 C, 15′-C, 21′-C), 34.5 (1 C, 2′-C), 35.3 (1 C, 30′-C), 35.6 (2 C, 19′-C, 21′-C), 35.8 (1 C, 1′-C), 39.7 (2 C, 16′-C, 22′-C), 42.0 (1 C, 6′-C), 42.9 (1 C, 18′-C), 50.0 (1 C, 4′-C), 53.7 (1 C, 8′-C), 60.9 (1 C, 5b-C), 61.1 (1 C, 6b-C), 61.8 (1 C, 10′-C), 65.9 (1 C, 5a-C), 67.8 (1 C, 4b-C), 68.0 (1 C, 4c-C), 69.3 (1 C, 6a-C), 70.2 (1 C, 2c-C), 70.4 (2 C, 2b-C, 3c-C), 70.6 (2 C, 3b-C, 5b-C), 76.8 (1 C, 2a-C), 79.4 (1 C, 4b-C), 80.2 (1 C, 3a-C), 85.1 (1 C, 3′-C), 98.4 (1 C, 1c-C), 99.0 (1 C, 1b-C), 102.2 (1 C, *C*HPh), 104.9 (1 C, 1a-C), 126.1, 128.3 (5 C, Ph), 138.2 (1 C, *ipso*-Ph), 169.0 (7 C, 7 CH_3*C*O). MALDI-MS: *m*/*z* = 1289 $[M + Na]^+$, 1306 $[M + K]^+$. $C_{68}H_{98}O_{22}$ (1267.5): calcd. C 64.44, H 7.79; found C 64.06, H 8.36.

3β-*O*-{(2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)]-(β-D-glucopyranosyl)}-friedelanol (54): A solution of **53** (109 mg, 0.09 mmol) in CH_2Cl_2 (8 mL) was treated with ethanethiol (0.8 mL, 0.011 mmol) and *p*-toluenesulfonic acid (catalytic amount) and stirred at room temp. After 2 h the solution was neutralized with triethylamine and concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1 → 1:2) to give **54** (64 mg,

60%). TLC (CH_2Cl_2/CH_3OH, 9:1): R_f = 0.60. $[\alpha]_D$ = –20.5 (c = 1, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$, ppm): δ = 0.83–0.87 (m, 4 H, 10′-H, 24′-CH_3), 0.90–0.93 (m, 5 H, 16′-H_a, 22′-H_a, 30′-CH_3), 0.94–0.95 (m, 4 H, 6′-H_a, 25′-CH_3), 0.96 (s, 3 H, 26′-CH_3) 0.98 (2s, 6 H, 29′-CH_3, 27′-CH_3) 1.01 (d $J_{23,4}$ = 7.0 Hz, 3 H,, 23′-CH_3), 1.07–1.55 (m, 23 H, 1′-H_a, 28′-CH_3, 19′-H_a, 11′-H_a, 4′-H, 15′-H_a, 21′-H_a, 8′-H, 12′-$H_{a,b}$, 7′-H_a, 19′-H_b, 11′-H_b, 2′-H_a, 15′-H_b, 21′-H_b, 16′-H_b, 22′-H_b, 7′-H_b, 18′-H, 1′-H_b), 1.71 (br. d, 1 H, 6′-H_b), 1.97 (s, 3 H, Ac), 2.04–2.05 (m, 11 H, 3 Ac, 5,6-OH), 2.07, 2.13, 2.15 (3s, 9 H, 3 Ac), 3.26 (dd, $J_{5,4}$ = 4.9, $J_{5,6}$ = 9.2 Hz, 1 H, 5a-H), 3.45–3.51 [m, 3 H, H,H-COSY: 3.46 (4a-H), 3.49 (5c-H_a), 3.50 (3′-H)], 3.63 (dd, $J_{3,2}$ = $J_{3,4}$ = 8.6 Hz, 1 H, 3a-H), 3.72 (br. s, 1 H, 6a-H_a), 3.79 (dd, $J_{2,3}$ = $J_{2,1}$ = 8.3 Hz, 1 H, 2a-H), 3.84–3.87 (m, 2 H, 5b-H, 6a-H_b), 4.08–4.17 (m, 2 H, 6b-$H_{a,b}$), 4.24–4.26 (m, 2 H, 1a-H, 5c-H_b), 4.84 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1b-H), 4.85 (d, $J_{1,2}$ = 6.1 Hz, 1 H, 1c-H), 4.99 (dd, $J_{4,3}$ = 6.9, $J_{4,5\text{-Ha}}$ = 12.2 Hz, 1 H, 4c-H), 5.05–5.10 (m, 2 H, 3b-H, 2c-H), 5.12–5.18 (m, 2 H, 2b-H, 3c-H), 5.34 (d, $J_{4,3}$ = 3.0 Hz, 1 H, 4b-H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 11.7 (1 C, 23′-C), 16.5, 16.6 (2 C, 25′-C, 7′-C), 18.3 (1 C, 24′-C), 18.6 (1 C, 27′-C), 20.1, 20.6, 20.7, 21.0 (8 C, 26′-C, 7 CH_3CO), 30.6 (1 C, 12′-C), 31.8 (1 C, 29′-C), 32.0 (1 C, 28′-C), 32.3 (2 C, 15′-C, 21′-C), 34.5 (1 C, 2′-C), 35.3 (1 C, 30′-C), 35.3 (2 C, 19′-C, 21′-C), 35.6 (1 C, 1′-C), 39.7 (2 C, 16′-C, 22′-C), 42.0 (1 C, 6′-C), 42.7 (1 C, 18′-C), 49.7 (1 C, 4′-C), 53.2 (1 C, 8′-C), 60.9 (1 C, 6b-C), 61.3 (1 C, 10′-C), 62.3 (1 C, 5c-C), 63.0 (1 C, 6a-C), 67.1 (1 C, 4b-C), 69.0 (1 C, 4c-C), 69.9 (2 C, 2a-C, 2b-C), 70.4 (1 C, 5b-C), 70.7 (1 C, 3b-C), 71.2 (2 C, 2c-C, 3c-C), 74.7 (1 C, 5a-C), 75.3 (1 C, 2a-C), 84.4 (1 C, 3′-C), 87.1 (1 C, 3a-C), 98.9 (1 C, 1b-C), 100.3 (1 C, 1c-C), 103.9 (1 C, 1a-C), 168.9, 169.7, 169.8, 170.0, 170.1, 170.3 (7 C, 7 CH_3CO). MALDI-MS (positive mode, matrix DHB, THF): m/z = 1201 $[M + Na]^+$. $C_{61}H_{94}O_{22}$ (1179.4): calcd. C 62.12, H 8.03; found C 61.83, H 8.21.

3β-*O*-{(β-D-Xylopyranosyl)-(1→3)-[(β-D-galactopyranosyl)-(1→2)]-(β-D-glucopyranosyl)}friedelanol (55): Compound **54** (23 mg, 0.02 mmol) dissolved in dry CH_3OH/CH_2Cl_2 (6:1, 12 mL) was treated with sodium methoxide (1 N solution in CH_3OH, 5 drops) and stirred at room temp. for 24 h. After neutralizing with ion-exchange resin (Amberlite IR-120 H^+), the resin was filtered off and the filtrate concentrated in vacuo. The residue was purified by flash chromatography (CH_2Cl_2/CH_3OH, 7:3) to afford **55** (17 mg, qu). TLC (CH_2Cl_2/CH_3OH, 7:3): R_f = 0.38. $[\alpha]_D$ = –3.3 (c = 1, $CHCl_3$/CH_3OH, 7:3). ^1H NMR (600 MHz, $CDCl_3$/CD_3OD, 5:1, ppm): δ = 0.59–0.62 (m, 4 H, 10′-H, 24′-CH_3), 0.65 (s, 3 H, 24′-CH_3), 0.78 (s, 3 H, 23′-CH_3), 0.82–0.83 (2s, 9 H, 30′-CH_3, 29′-CH_3, 27′-CH_3), 0.98 (s, 3 H, 27′-CH_3), 1.23 (s, 3 H, 28′-CH_3), 0.84–2.00 (m, 22 H), 2.23–2.39 (m, 1 H, 2′-H_b), 3.21–3.30 [m, 4 H, H,H-COSY: 3.21 (5c-H_a), 3.23 (5a-H), 3.26 (2c-H), 3.29 (3c-H), 3.37 (dd, $J_{4,3}$ = $J_{4,5}$ ≈ 8.0 Hz, 1 H, 4a-H), 3.44–3.59 [m, 6 H, H,H-COSY: 3.44 (3b-H), 3.47 (5b-H), 3.50 (2b-H), 3.52 (4c-H), 3.54 (3a-H), 3.58 (2a-H)], 3.64–3.67 (m, 2 H, 3′-H, 6a-H_a), 3.73–3.75 (m, 2 H, 6b-$H_{a,b}$), 3.82 (dd, J_{gem} ≈ 10.7, $J_{6,5}$ < 1.0 Hz, 1 H, 6a-H_b), 3.87–3.91 (m, 2 H, 4b-H, 5c-H_b), 4.44 (d, $J_{1,2}$ = 7.3 Hz, 1 H, 1c-H), 4.48 (d, $J_{1,2}$ = 7.6 Hz, 1 H, 1a-H), 4.60 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1b-H). ^{13}C NMR (151 MHz, $CDCl_3$/CD_3OD, 5:1, ppm): δ = 55.0 (1 C, 10′-C), 61.2 (1 C, 6b-C), 62.1 (1 C, 6a-C), 66.1 (1 C, 5c-C), 69.0 (2 C, 4b-C, 4a-C), 69.7 (1 C, 4c-C), 72.5 (1 C, 2b-C), 73.5 (1 C, 3b-C), 73.8 (1 C, 2c-C), 75.3 (1 C, 5b-C), 76.1 (1 C, 5a-C), 77.3 (1 C, 3c-C), 79.7 (1 C, 3′-C), 80.3 (1 C, 2a-C), 86.2 (1 C, 3a-C), 100.9 (1 C, 1a-C), 103.9 (1 C, 1b-C), 104.4 (1 C, 1c-C). MALDI-MS (positive mode, matrix DHB, CH_3OH): m/z = 909 $[M + Na]^+$. $C_{47}H_{80}O_{15}$ (885.1).

3β-*O*-{(2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→2)]-(6-β-D-glucopyranosyl uronic acid)}friedelanol (56): To a mixture of compound **54** (14 mg, 11.6 μmol), NaBr (204 μg, 2.0 μmol), TBABr (208 μg, 0.6 μmol) and TEMPO (161 μg, 10.3 μmol) in CH_2Cl_2/H_2O (6:1, 0.25 mL) cooled to 0 °C was added a mixture of NaOCl (0.05 mL), H_2O (0.04 mL), $NaHCO_3$ (0.07 mL). After stirring for 30 min was added methanol (0.08 mL). The compound was extracted in CH_2Cl_2 and the solvent evaporated to give a residue, which was purified by flash chromatography (CH_2Cl_2/CH_3OH, 9:1 → 5:1) to afford **56** (11 mg, 76%). TLC (CH_2Cl_2/CH_3OH, 9:1): R_f = 0.09. $[\alpha]_D$ = +1.6 (c = 0.5, CH_3OH). ^1H NMR (600 MHz, $CDCl_3$/CD_3OD, 5:1, ppm): δ = 0.78–0.82 (m, 4 H, 10′-H, 24′-CH_3), 0.86–0.88 (m, 5 H, 16′-H_a, 22′-H_a, 30′-CH_3), 0.89–0.90 (m, 4 H, 6′-H_a, 25′-CH_3), 0.91 (s, 3 H, 26′-CH_3) 0.93, 0.94 (2s, 6 H, 29′-CH_3, 27′-CH_3) 0.98 (d $J_{23',4'}$ = 7.3 Hz, 3 H,, 23′-CH_3), 1.02–1.62 (m, 23 H, 1′-H_a, 28′-CH_3, 19′-H_a, 11′-H_a, 4′-H, 15′-H_a, 21′-H_a, 8′-H, 12′-$H_{a,b}$, 7′-H_a, 19′-H_b, 11′-H_b, 2′-H_a, 15′-H_b, 21′-H_b, 16′-H_b, 22′-H_b, 7′-H_b, 18′-H, 1′-H_b), 1.65 (br. d, 1 H, 6′-H_b), 1.91, 2.01, 2.02 (4s, 18 H, 6 Ac), 2.10–2.11 (m, 4 H, 2′-H_b, Ac), 2.15 (s, 3 H, Ac), 3.43–3.46 (m, 2 H, 5c-H_a, 3′-H), 3.67–3.69 (m, 2 H, 3a-H, 5a-H), 3.72–3.75 (m, 1 H, 4a-H), 3.81–3.87 [m, 2 H, H,H,-COSY: 3.82 (2a-H), 3.87 (1 H, 5b-H)], 4.06–4.09 (m, 2 H, 6b-$H_{a,b}$), 4.22 (d, $J_{1,2}$ = 7.5 Hz, 1 H, 1a-H), 4.34 (dd, $J_{5,4}$ = 4.2, J_{gem} = 12.5 Hz, 1 H, 5c-H_b), 4.83 (d, $J_{1,2}$ = 7.6 Hz, 1 H, 1b-H), 4.86–4.90 (m, 1 H, 4c-H), 4.92 (d, $J_{1,2}$ = 4.5 Hz, 1 H, 1c-H), 4.99 (dd, $J_{2,1}$ = 4.5, $J_{2,3}$ = 6.6 Hz, 1 H, 2c-H), 5.02–5.07 (m, 2 H, 2b-H, 3c-H), 5.09–5.11 (dd, $J_{3,2}$ = 13.9, $J_{3,4}$ = 3.4 Hz, 1 H, 3b-H), 5.30 (br. d, 1 H, 4b-H). ^{13}C NMR (151 MHz, $CDCl_3$/CD_3OD, 5:1, ppm): δ = 13.6 (1 C, 23′-C), 16.5, 16.6 (2 C, 25′-C, 7′-C), 18.3 (1 C, 24′-C), 18.6 (1 C, 27′-C), 20.1, 20.4 (8 C, 26′-C, 7 CH_3CO), 30.6 (1 C, 12′-C), 31.4 (1 C, 29′-C), 31.8 (1 C, 28′-C), 32.3 (2 C, 15′-C, 21′-C), 34.1 (1 C, 2′-C), 34.9 (1 C, 30′-C), 35.0 (2 C, 19′-C, 21′-C), 35.4 (1 C, 1′-C), 39.2 (2 C, 16′-C, 22′-C), 42.0 (1 C, 6′-C), 42.7 (1 C, 18′-C), 49.7 (1 C, 4′-C), 52.8 (1 C, 8′-C), 60.7 (2 C, 5c-C, 6b-C), 61.0 (1 C, 10′-C), 67.2 (1 C, 4b-C), 68.0 (1 C, 4c-C), 69.8 (1 C, 4a-C), 69.9 (3 C, 2b-C, 2c-C, 3c-C), 70.3 (1 C, 5b-C), 70.3 (1 C, 3b-C), 73.9 (1 C, 5a-C), 75.7 (1 C, 2a-C), 83.2 (1 C, 3a-C), 84.6 (1 C, 3′-C), 98.4 (1 C, 1c-C), 98.5 (1 C, 1b-C), 103.9 (1 C, 1a-C). MALDI-MS (positive mode, matrix DHB, CH_3OH): m/z = 1218 $[M + Na]^+$. $C_{61}H_{92}O_{23}$ (1193.4).

3β-*O*-{(β-D-Xylopyranosyl)-(1→3)-[(β-D-galactopyranosyl)-(1→2)]-(6-β-D-glucopyranosyl uronic acid)}friedelanol (2): Compound **56** (17 mg, 14.4 μmol) dissolved in dry CH_3OH (5 mL) was treated with sodium methoxide (1 N solution in CH_3OH, 10 drops) and stirred at room temp. for 12 h. After neutralization with ion-exchange resin (Amberlite IR-120 H^+), the resin was filtered off and the filtrate concentrated in vacuo. The residue was purified by flash chromatography (CH_2Cl_2/CH_3OH, 2:1 → 1:1 → 1:2) to afford **2** (8 mg, 62%). TLC (CH_2Cl_2/CH_3OH, 2:1): R_f = 0.20. $[\alpha]_D$ = +0.9 (c = 0.1, CH_3OH). ^1H NMR (600 MHz, CD_3OD/D_2O, 5:1, ppm): δ = 0.84–0.85 (m, 4 H, 10′-H, 24′-CH_3), 0.89–1.00 (m, 21 H, 16′-H_a, 22′-H_a, 30′-CH_3, 6′-H_a, 25′-CH_3, 26′-CH_3, 29′-CH_3, 27′-CH_3, 23′-CH_3), 1.10–1.58 (m, 23 H, 1′-H_a, 28′-CH_3, 19′-H_a, 11′-H_a, 4′-H, 15′-H_a, 21′-H_a, 8′-H, 12′-$H_{a,b}$, 7′-H_a, 19′-H_b, 11′-H_b, 2′-H_a, 15′-H_b, 21′-H_b, 16′-H_b, 22′-H_b, 7′-H_b, 18′-H, 1′-H_b), 1.73 (br. d, 1 H, 6′-H_b), 2.13–2.28 (m, 1 H, 2′-H_b), 3–26–3.34 [m, 3 H, H,H-COSY: 3.26 (5c-H_a), 3.28 (2c-H), 3.34 (3c-H)], 3.49–3.61 [m, 6 H, H,H-COSY: 3.48 (3b-H), 3.50 (5b-H), 3.51 (2b-H), 3.53 (4c-H), 3.59 (4a-H), 3.60 (5a-H)], 3.69–3.72 (m, 3 H, 6b-$H_{a,b}$, 3a-H), 3.85–3.94 [m, 3 H, H,H-COSY: 3.85 (4b-H), 3.88 (2a-H), 3.93 (5c-H_b)], 4.38–4.86 [m, 3 H, H,H-COSY: 4.38 (1a-H), 4.60 (1c-H), 4.86 (1b-H)]. ^{13}C NMR (151 MHz, CD_3OD/D_2O, 5:1, ppm): δ = 12.3 (1 C, 23′-C), 17.3 (2 C, 25′-C, 7′-C), 18.9 (1 C, 24′-C), 19.3 (1 C, 27′-C), 20.1, 20.8 (1 C, 26′-C), 30.0 (1 C, 12′-C), 31.0 (1 C, 29′-C), 31.3 (1 C, 28′-C), 33.5 (2 C, 15′-C, 21′-C), 34.9 (1 C, 2′-C), 35.4

(1 C, 30′-C), 36.2 (2 C, 19′-C, 21′-C), 36.4 (1 C, 1′-C), 40.0 (2 C, 16′-C, 22′-C), 42.8 (1 C, 6′-C), 44.0 (1 C, 18′-C), 50.3 (1 C, 4′-C), 53.8 (1 C, 8′-C), 61.4 (1 C, 6b-C), 62.0 (1 C, 10′-C), 66.6 (1 C, 5c-C), 69.4 (1 C, 4b-C), 70.2 (1 C, 4c-C), 70.4 (1 C, 4a-C), 73.0 (1 C, 2b-C), 74.3 (1 C, 3b-C), 74.5 (1 C, 2c-C), 76.0 (1 C, 5b-C), 77.4 (1 C, 3c-C), 78.1 (1 C, 2a-C), 84.4 (1 C, 5a-C), 86.2 (1 C, 3a-C), 103.1 (1 C, 1b-C), 104.1 (1 C, 1c-C), 105.1 (1 C, 1a-C). MALDI-MS (positive mode, matrix DHB, CH_3OH): m/z = 921 $[M + Na]^+$, 938 $[M + K]^+$. $C_{47}H_{78}O_{16}\cdot 5.5H_2O$ (998.2): calcd. C 56.55, H 8.98; found C 56.52, H 9.42.

Acknowledgments

This work was supported by the Ludwig Institute for Cancer Research, New York, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie. We are grateful to Professor Armin Geyer and to Anke Friemel for their help with the structural assignments and Dr. Karl-Heinz Jung for his help in preparing the manuscript.

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Received: October 18, 2005
Published Online: February 3, 2006

