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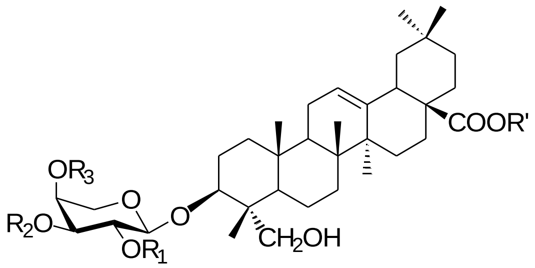

R_1, R_2, R_3 = H, β-D-Xyl, β-D-Glc

R' = H, CH_3

The synthesis of eight L-arabinopyranose containing hederagenin saponins, five of which are natural products, and their methyl esters is described.

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Abstract

The synthesis of eight hederagenin saponins, five of which are natural products, and their methyl esters is described as part of an ongoing study of the biological activity of triterpenoid saponins. Six disaccharides consisting of an L-arabinopyranose glycosylated in positions 2, 3, or 4 with a β-D-xylopyranose or a β-D-glucopyranose residue respectively, were synthesized in good to excellent yields. The saponins were then prepared in good yields through glycosylation with a suitably protected hederagenin derivative followed by total deprotection and treatment with diazomethane.

1. Introduction

Saponins are triterpene or steroid glycosides which are found in a wide variety of plants and certain marine organisms.[1] Interest in saponins is rapidly increasing due to their numerous biological properties,[2,3] but a limiting factor in their evaluation is often the small amounts obtained from natural product extraction. Chemical synthesis offers an alternative to saponin extraction in plants, and opens the door to the preparation of tailor-made molecules. In the study of saponin structure-activity relationships, both the aglycone and the sugar moiety play an important role in the evaluation of biological activity and must be considered individually. It is thus essential to have access to all the positional isomers of a given sugar moiety while keeping the aglycone constant. We have implemented this strategy as part of our ongoing study of the hemolytic activity of hemi-synthetic hederagenin saponins in an attempt to better understand the role of the sugar moiety on hemolysis.[4] Having previously synthesized α-hederin and its positional isomers with respect to the L-rhamnopyranosyl-L-arabinopyranose disaccharide moiety[5] the synthesis of two additional families of hederagenin saponins was undertaken (Figure 1). While keeping an L-arabinopyranose as the first sugar, a D-xylopyranose and a D-glucopyranose were chosen as the second one in the disaccharide moiety. In total, we wished to synthesize eight hederagenin saponins including **2** and **6** having a β configuration between the aglycone and the sugar chain, normally not found in natural sources. Five

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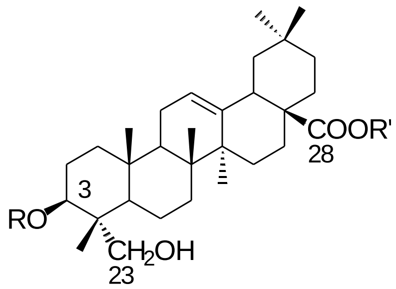
of the eight saponins are naturally occurring in plants (**1**, **3**, **5**, **7**, **8**),[1,6] and several of the saponins have shown molluscicidal[6b,7] (**3**, **5**), hemolytic[8] (**5**), and cytotoxic[9] (**5**,**7**) activities.



R = β-D-Xyl-(1→2)-α-L-Ara	R' = H (**1**) R' = CH_3 (**1a**)	R = β-D-Glc-(1→2)-α-L-Ara	R' = H (**5**) R' = CH_3 (**5a**)
R = β-D-Xyl-(1→2)-β-L-Ara	R' = H (**2**) R' = CH_3 (**2a**)	R = β-D-Glc-(1→2)-β-L-Ara	R' = H (**6**) R' = CH_3 (**6a**)
R = β-D-Xyl-(1→3)-α-L-Ara	R' = H (**3**) R' = CH_3 (**3a**)	R = β-D-Glc-(1→3)-α-L-Ara	R' = H (**7**) R' = CH_3 (**7a**)
R = β-D-Xyl-(1→4)-α-L-Ara	R' = H (**4**) R' = CH_3 (**4a**)	R = β-D-Glc-(1→4)-α-L-Ara	R' = H (**8**) R' = CH_3 (**8a**)

Figure 1. D-Xyl-L-Ara and D-Glc-L-Ara hederagenin saponins

While the synthesis of steroidal saponins has been widely reported in the literature,[10] that of triterpenoid saponins has attracted less attention. A large majority of triterpenoid saponin syntheses involve oleanolic acid as the aglycone,[11] and the use of others remains rare (e.g. hederagenin,[5] glycyrrhetic acid,[12] ursolic acid,[13] or medicagenic acid[14]).

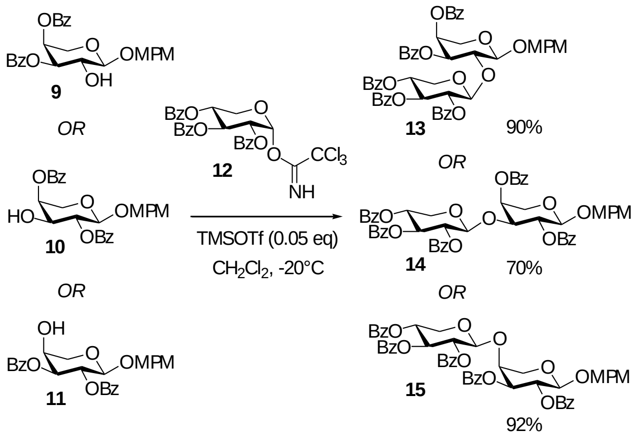
Few examples exist in the literature concerning the synthesis of disaccharides with an L-arabinopyranose at the reducing end. In the β-D-xylopyranosyl-α-L-arabinopyranose series, several syntheses have been reported for the disaccharide portion of the saponin OSW-1 (β-D-Xyl-(1→3)-α-L-Ara).[15] Deng *et al.* originally reported the use of a benzyl L-arabinopyranose precursor with free hydroxyl groups in positions 3 and 4 and a trichloroacetimidate derivative of β-D-xylopyranose giving a mixture of disaccharides with glycosylation in position 3 being the predominant reaction.[15e] The same authors also reported that glycosylation of a phenyl 1-thio-L-arabinopyranose precursor with free hydroxyl groups in positions 3 and 4 resulted in the β-D-Xyl-(1→4)-α-L-Ara disaccharide as the major reaction product.[16] In the synthesis of Yu *et al.*[15c] the target disaccharide β-D-Xyl-(1→3)-α-L-Ara was prepared in 93% yield from a protected L-arabinopyranose derivative and a D-xylopyranosyl trichloroacetimidate.

In the β-D-glucopyranose-α-L-arabinopyranose series, Liptak *et al.* described the first synthesis of a β-D-glucopyranosyl-(1→2)-α-L-arabinopyranose disaccharide derivative in 1982 as part of a ^{13}C NMR spectroscopy study of methyl and benzyl β-L-arabinopyranose oligosaccharides.[17] The disaccharide was synthesized in low yield using a suitably protected benzyl β-L-arabinopyranose derivative and an acetobromoglucose in the presence of an excess of mercury cyanide. More recently, Field *et al.* reported the synthesis of two D-glucopyranose-L-arabinopyranose disaccharides which are fragments of the oat root saponin Avenacin A-1.[18] The desired disaccharides were synthesized in good yields using a thioglycoside donor.

We wish to describe here the efficient synthesis of β-D-xylopyranosyl-α-L-arabinopyranose and β-D-glucopyranosyl-α-L-arabinopyranose disaccharides and their use in the synthesis of eight hederagenin saponins and their methyl esters as part of a directed study of the hemolytic activity of hederagenin saponins. To our knowledge, this is the first reported synthesis of β-D-Xyl-(1→2)-α-L-Ara and β-D-Glc-(1→3)-α-L-Ara disaccharides as well as that of eight hederagenin saponins, five of which are natural products.

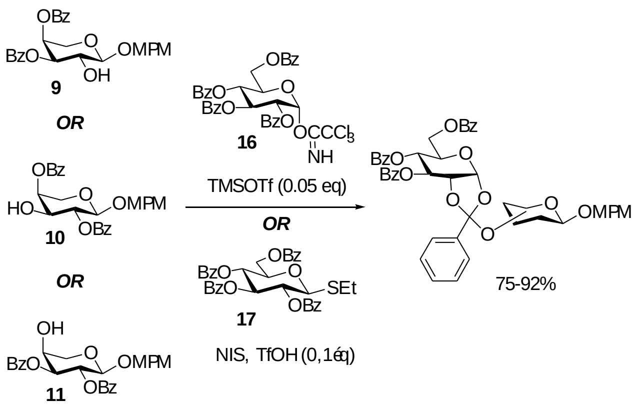
2. Results and Discussion

The previously described L-arabinopyranose derivatives **9**, **10** and **11** were the starting point for the disaccharide syntheses.[5] In the D-xylopyranose series, glycosylation with 2,3,4-tri-*O*-benzoyl-α-D-xylopyranosyl trichloroacetimidate[19] (**12**) gave the desired disaccharides in good to excellent yields (Scheme 1).



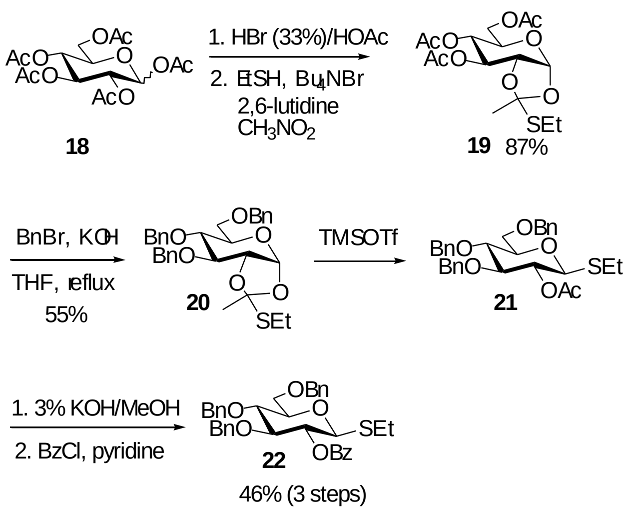
Scheme 1

When the same glycosylation strategy was tried in the D-glucopyranose series using 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (**16**),[20] the reaction resulted in the isolation of the corresponding orthoesters in good yields (75%-92%) with no trace of the desired disaccharides (Scheme 2). Modifying the reaction conditions or attempting orthoester opening with excess TMSOTf or $HgBr_2$ resulted in total degradation of the starting material. The use of the corresponding per-*O*-benzoylated thioglycoside donor **17**[21] was also tried with the arabinopyranose acceptor **10**. Once again, the orthoester was isolated in good yield.



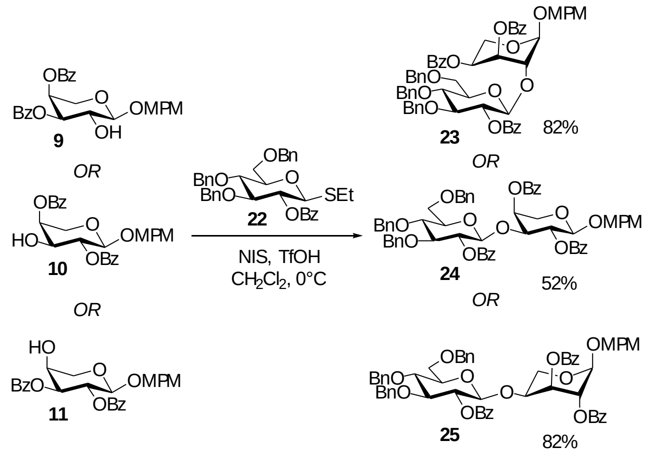
Scheme 2

Ethyl 2-*O*-benzoyl-3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (**22**) was then synthesized using an analogous procedure described for D-galactose (Scheme 3).[22] By replacing the benzoate protecting groups in positions 3, 4, and 6 with benzyl groups we hoped to enhance the reactivity of the thioglycoside donor, and avoid, if possible, further orthoester formation.



Scheme 3

Compound **22** was then successfully used as a donor in the glycosylation reactions with the arabinopyranose acceptors **9**, **10,** and **11**. The disaccharides were obtained in good to moderate yields with no detectable orthoesters in the reaction mixtures (Scheme 4).

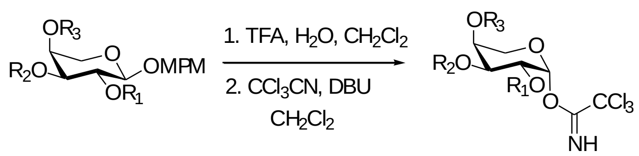


Scheme 4

One possible explanation for the moderate yield of disaccharide **24** could be the steric hindrance created by the addition of a D-glucopyranose in position 3 of the L-arabinopyranose derivative **10**. Optimization of the glycosylation reaction at different temperatures or by the addition of a larger quantity of the thioglycoside donor (up to 3 equivalents) did not increase the yield.

The anomeric MPM protecting groups of the disaccharides (**13-15**, **23-25**) were then removed in the presence of aqueous trifluoroacetic acid at room temperature. The resulting hemiacetal was reacted with trichloroacetonitrile in the presence of DBU, giving good to excellent yields of the corresponding trichloroacetimidates (Table 1).

Table 1. Trichloroacetimidate formation

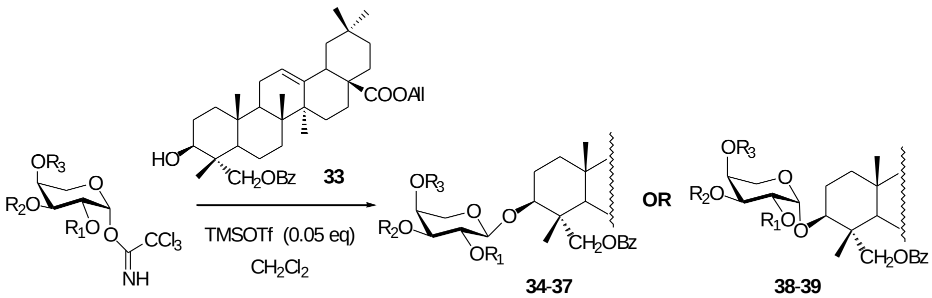


Disaccharide	R_1	R_2	R_3	Trichloroacetimidate	Yield
13	**Xyl**[a]	OBz	Bz	**27**	89%
14	Bz	**Xyl**	Bz	**28**	80%
15	Bz	Bz	**Xyl**	**29**	83%
23	**Glc**[b]	Bz	Bz	**30**	78%
24	Bz	**Glc**	Bz	**31**	74%
25	Bz	Bz	**Glc**	**32**	77%

[a] **Xyl** = (2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)
[b] **Glc** = (2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)

Saponin synthesis was then performed with the activated disaccharides **27-32** and the previously described allyl hederagenate derivative **33**.[5] Coupling at low temperature in the presence of a catalytic amount of TMSOTf gave the protected saponins in excellent yields (Table 2).

Table 2. Hederagenin glycosylation



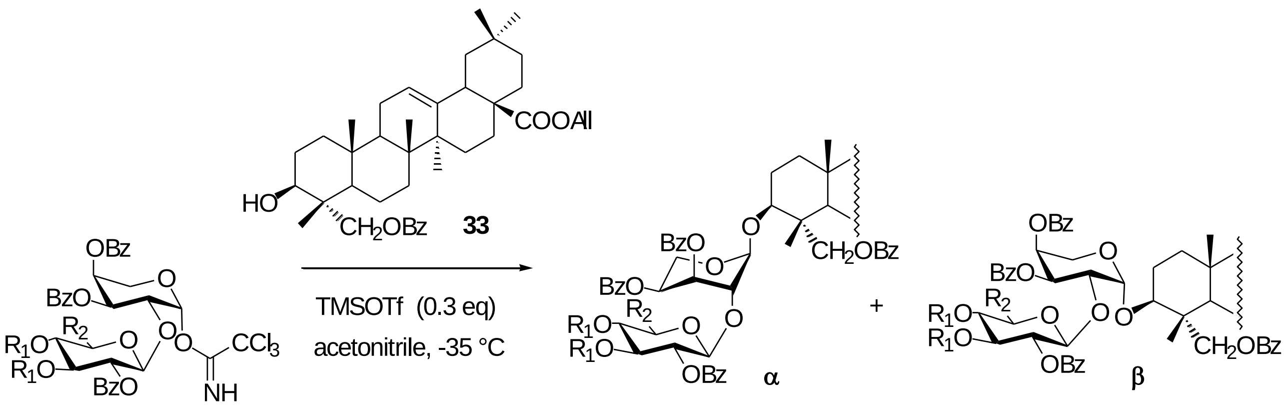
Trichloroacetimidate	R_1	R_2	R_3	Protected saponin	Yield
28	Bz	**Xyl**[a]	Bz	**34**	95%
29	Bz	Bz	**Xyl**	**35**	94%
31	Bz	**Glc**[b]	Bz	**36**	93%
32	Bz	Bz	**Glc**	**37**	95%
27	**Xyl**	Bz	Bz	**38**	94%
30	**Glc**	Bz	Bz	**39**	85%

[a] **Xyl** = (2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)
[b] **Glc** = (2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)

As expected, the presence of a benzoate in position 2 of the L-arabinopyranose moiety directed the glycosylation reaction and gave exclusive formation of the α anomers as a result of neighboring group participation. For the trichloroacetimidates **27** and **30** possessing a sugar residue in position 2, the β anomers were isolated as the major reaction products.

To prepare the corresponding α anomers of these two saponins, the coupling reaction was carried out in acetonitrile. Use of this solvent is known to promote equatorial bond formation in glycoside synthesis when neighboring group participation is absent.[23] Glycosylation with 2 equivalents of the donor in acetonitrile at -35°C gave a mixture of anomers with the desired α anomer being the major reaction product in both cases (Table 3).

Table 3. Glycosylation in acetonitrile

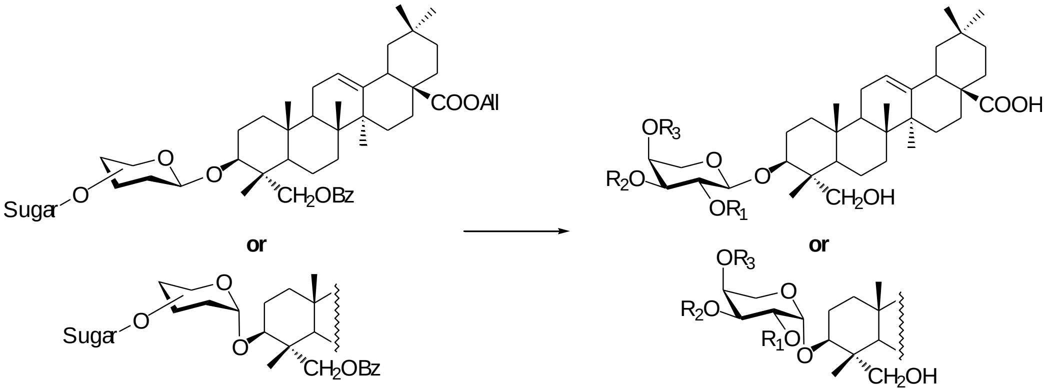


Trichloroacetimidate	R_1	R_2	Protected saponin (α)	Yield	H-1Ara: $J_{1,2}$ (Hz)	H-4Ara: $J_{4,5a}$ (Hz)	$J_{4,5b}$ (Hz)
27	Bz	H	**40**	58% (α) + 6% (β)	3.5	3.2	7.1
30	Bn	CH_2OBn	**41**	61% (α) + 14% (β)	nd	nd	6.4

Separation of the two anomers was possible by reverse phase HPLC in 100% acetonitrile. Based on the ^{1}H NMR coupling constants of the major α anomers ($J_{1,2}$, $J_{4,5a}$ and $J_{4,5b}$), it was observed that for compound **40** with a D-xylopyranosyl-L-arabinopyranose side chain the arabinopyranose ring adopts a $^1C_4$ conformation to relieve steric hindrance. In the case of the saponin with a D-glucopyranose-L-arabinopyranose side chain (**41**) the situation is not as clear-cut as several coupling constants remain undetermined.

Total deprotection of the saponin derivatives was performed in one or two steps based on the starting compound. While having previously reported the efficient removal of a hederagenin allyl ester in the presence of pyrrolidine and catalytic amounts of tetrakis(triphenylphosphine) palladium(0) [$Pd(PPh_3)_4$],[4,5] we sought to reduce the somewhat long reaction times necessary to achieve complete deprotection. In a normal de-allylation reaction, excess pyrrolidine serves as a nucleophile, driving the reaction to completion.[24] A recent literature example describes the deprotection of allylphenols in a 10% KOH/MeOH solution in the presence of a catalytic amount of Pd/C.[25] We felt that replacing the pyrrolidine with an excess of KOH could lead to the deprotection of both the allyl and benzoyl protecting groups in one step. It was found that heating the saponin in the presence of 1 equivalent of $Pd(PPh_3)_4$ in a 3% KOH solution in methanol at 60° C for 6 hours afforded the completely deprotected D-xylopyranosyl-L-arabinopyranose saponins (**1-4**) or the partially protected D-glucopyranosyl-L-arabinopyranose ones in good yield. For the latter compounds, the benzyl groups were then removed by hydrogenolysis in the presence of Pd/C at atmospheric pressure (Table 4). Hydrogenolysis or migration of the double bond in the triterpenoid skeleton was not observed using these reaction conditions. Successful deprotection was also possible with a catalytic amount of $Pd(PPh_3)_4$ (0.3 eq) in a mixture of THF/3% KOH/MeOH at 60 °C, with the desired saponins being isolated in fair to excellent yields. The use of as little as 0.1 eq of $Pd(PPh_3)_4$ was tried for the D-xylopyranose-L-arabinopyranose saponins, but in most cases the yields were poorer than those obtained with 0.3 eq of catalyst.

Table 4. Total deprotection of saponins: optimization of reaction conditions



method A : 3% KOH/MeOH or THF/3% KOH/MeOH, $Pd(PPh_3)_4$, 60 °C

method B : 1. 3% KOH/MeOH or THF/3% KOH/MeOH, $Pd(PPh_3)_4$, 60 °C; 2. Pd/C, H_2

Protected saponin	Deprotection Method	Saponin	R_1	R_2	R_3	Yield (1eq Pd) [c]	Yield (0.3eq Pd) [d]	Yield (0.1eq Pd) [d]
40	A	**1**	**Xyl**[a]	H	H	76%	89%	64%
38	A	**2**	**Xyl**	H	H	64%	84%	88%
34	A	**3**	H	**Xyl**	H	82%	72%	71%
35	A	**4**	H	H	**Xyl**	84%	74%	66%
41	B	**5**	**Glc**[b]	H	H	82%	87%	---
39	B	**6**	**Glc**	H	H	88%	82%	---
36	B	**7**	H	**Glc**	H	78%	84%	---
37	B	**8**	H	H	**Glc**	82%	65%	---

[a] **Xyl** = (β-D-xylopyranosyl)
[b] **Glc** = (β-D-glucopyranosyl)
[c] 3% KOH/MeOH, 60 °C
[d] THF/3% KOH/MeOH, 60 °C

The corresponding methyl esters (**1a-8a**) were then prepared in quantitative yield by diazomethane treatment of the acids **1-8**.[26]

3. Conclusion

Efficient chemical synthesis afforded a rapid access to eight hederagenin saponins, five of which are naturally occurring products whose synthesis has not yet been reported in the literature. The synthesis of six disaccharides consisting of an L-arabinopyranose substituted in positions 2, 3, or 4 with a β-D-xylopyranose or a β-D-glucopyranose residue was accomplished in good to excellent yields. Coupling of these disaccharides to a protected hederagenin derivative and total deprotection gave the desired saponins in 52%-79% overall yields. A deprotection method was developed with $Pd(PPh_3)_4$ in the presence of KOH to efficiently remove both the allyl ester and the sugar benzoyl protecting groups in one step. The fully deprotected saponins were thus obtained in good yields with significantly shorter reaction times.

The preparation of triterpenoid saponins in larger quantities facilitates the study of their biological activity. The strategy presented here opens the door to the synthesis of a wide variety of different saponins by simply changing the nature of the aglycone. In addition, structure-activity relationships can be more easily studied when all the positional isomers of a given sugar moiety are readily accessible. The hemolytic and cytotoxic activity of these molecules will be reported in due course.

4. Experimental

4.1. General Methods

All chemicals were reagent grade and used as supplied unless otherwise noted. Dichloromethane (CH_2Cl_2) and triethylamine were refluxed over calcium hydride and distilled prior to use. All reactions were performed under an Argon atmosphere unless otherwise indicated. Analytical thin-layer chromatography (TLC) was performed on E. Merck Silica Gel 60 F_{254} plates. Compounds were visualized by dipping in an anisaldehyde solution in ethanol and heating. Column chromatography was performed using E. Merck Geduran Silica Gel Si 60 (40-60 µM). Optical rotations were recorded at 22 °C with a Perkin-Elmer 241 polarimeter. ESI-MS were recorded with a Thermofinnigan quadripolar mass spectrometer with positive ion data collected automatically. High Resolution mass spectra were recorded on a Micromass Q-TOF spectrometer. NMR spectra were obtained using a Bruker Avance DRX 500 spectrometer (500 MHz for ^1H and 125 MHz for ^{13}C). Elemental analyses were performed on a Perkin-Elmer CHN 2400. The HPLC system (Shimadzu) consisted of a solvent delivery system equipped with dual pumps (LC-8A), and a UV spectrophotometric detector (SPD-6A). Preparative HPLC was performed using a Merck

Hibar column (250 mm × 25 mm; Lichrospher RP 18 (7μm)). Protected saponins were detected at 230 nm.

4.2. 4-Methoxybenzyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-arabinopyranoside (13). General Method. In a typical experiment, 4-methoxybenzyl 3,4-di-*O*-benzoyl-α-L-arabinopyranoside[5] **9** (1.5 g, 3.1 mmol), 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl trichloroacetimidate[19] **12** (2.85 g, 4.7 mmol, 1.5 eq) and 4 Å powdered molecular sieves (6 g) were stirred for 1h at room temperature in CH_2Cl_2 (75 mL). The mixture was cooled to –20 °C for 30 minutes followed by the dropwise addition of a 0.1 M solution of TMSOTf in CH_2Cl_2 (1.55 mL, 0.16 mmol, 0.05 eq). After stirring for 2h at this temperature, the reaction was quenched with triethylamine (0.5 mL), filtered through Celite and evaporated. The crude residue was purified by column chromatography (toluene/acetone 99:1 to 98:2) to give 2.62 g (90%) of disaccharide **13** as an amorphous solid. R_f = 0.47 (toluene/acetone 9:1). $[\alpha]_D$ = +32.9° (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 3.70 (dd, 1H, *J* = 12.7, *J* = 5.3 Hz, H-5'), 3.85 (s, 3H, OCH_3), 3.91 (dd, 1H, *J* = 12.3, *J* = 2.1 Hz, H-5), 4.29 (dd, 1H, *J* = 12.4, *J* = 4.7 Hz, H-5), 4.39 (dd, 1H, *J* = 7.3, *J* = 5.5 Hz, H-2), 4.57 (dd, 1H, *J* = 12.8, *J* = 3.7 Hz, H-5'), 4.64 (d, 1H, *J* = 10.9 Hz, CH_2MPM), 4.88 (d, 1H, *J* = 5.3 Hz, H-1), 4.98 (d, 1H, *J* = 10.9 Hz, CH_2MPM), 5.25 (d, 1H, *J* = 4.2 Hz, H-1'), 5.28 (m, 1H, H-4'), 5.35 (dd, 1H, *J* = 6.2, *J* = 4.3 Hz, H-2'), 5.53 (dd, 1H, *J* = 7.5, *J* = 3.4 Hz, H-3), 5.56 (m, 1H, H-4), 5.71 (t, 1H, *J* = 6.3 Hz, H-3'), 6.91 (d, 2H, *J* = 8.6 Hz, Ar-H), 7.21 (t, 1H, *J* = 7.7 Hz, Ar-H), 7.27 (t, 2H, *J* = 7.7 Hz, Ar-H), 7.36-7.49 (m, 11 H, Ar-H), 7.59 (m, 2H, Ar-H), 7.73 (d, 2H, *J* = 7.5 Hz, Ar-H), 7.86 (d, 2H, *J* = 7.3 Hz, Ar-H), 7.99 (d, 2H, *J* = 7.2 Hz, Ar-H), 8.05 (d, 2H, *J* = 7.0 Hz, Ar-H), 8.06 (d, 2H, *J* = 7.0 Hz, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 55.3 (OCH_3), 60.8 (C-5'), 61.5 (C-5), 68.0 (C-4), 68.7 (C-4'), 69.2 (C-3'), 69.8 (C-2'), 70.7 (CH_2MPM), 71.8 (C-3), 74.5 (C-2), 99.7 (C-1'), 100.1 (C-1), 113.8 (CH), 128.1 (CH), 128.3 (CH), 128.4 (CH), 128.4 (CH), 128.4 (CH), 128.8 (C), 129.0 (C), 129.1 (C), 129.3 (C), 129.4 (C), 129.6 (CH), 129.7 (CH), 129.8 (CH), 129.9 (CH), 129.9 (CH), 133.0 (C), 133.2 (C), 133.3 (C), 133.4 (C), 159.4 (C), 164.8 (CO), 165.1 (CO), 165.4 (CO), 165.4 (CO), 165.5 (CO). Anal. Calcd for $C_{53}H_{46}O_{15}$: C, 68.97; H, 5.02. Found: C, 68.60; H, 4.97.

4.3. 4-Methoxybenzyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-arabinopyranoside (14). This compound was prepared using the general method described for **13.** Reaction of 4-methoxybenzyl 2,4-di-*O*-benzoyl-α-L-arabinopyranoside **10**[5] (0.5 g, 1.0 mmol) and trichloroacetimidate **12** (0.95 g, 1.6 mmol) gave 0.68 g (70%) of **14**. R_f = 0.47 (toluene/acetone 9:1). $[\alpha]_D$ = +10.5° (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 3.67 (dd, 1H, *J* = 12.4, *J* = 5.8 Hz, H-5'), 3.75 (dd, 1H, *J* = 12.5, *J* = 2.2 Hz, H-5), 3.79 (s, 3H, OCH_3), 4.32 (dd, 1H, *J* = 7.8, *J* = 3.3 Hz, H-3), 4.35 (m, 2H, H-5, H-5'), 4.52 (d, 1H, *J* = 12.2 Hz, CH_2MPM), 4.63 (d, 1H, *J* = 5.7 Hz, H-1), 4.67 (d, 1H, *J* =

12.2 Hz, CH_2MPM), 5.16 (d, 1H, J = 4.7 Hz, H-1'), 5.22 (m, 1H, H-4'), 5.34 (dd, 1H, J = 6.6, J = 5.0 Hz, H-2'), 5.56 (m, 1H, H-4), 5.62 (dd, 1H, J = 7.5, J = 6.0 Hz, H-2), 5.65 (t, 1H, J = 6.6 Hz, H-3'), 6.71 (d, 2H, J = 8.5 Hz, Ar-H), 7.07 (d, 2H, J = 8.5 Hz, Ar-H), 7.20-7.63 (m, 15H, Ar-H), 7.81 (d, 2H, J = 7.6 Hz, Ar-H), 7.95 (m, 4H, Ar-H), 8.01 (d, 2H, J = 7.5 Hz, Ar-H), 8.15 (d, 2H, J = 7.4 Hz, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 55.1 (OCH_3), 60.9 (C-5'), 61.7 (C-5), 68.8 (C-4'), 69.3 (CH_2MPM), 69.7 (C-4, C-3'), 70.0 (C-2'), 70.8 (C-2), 76.5 (C-3), 98.4 (C-1), 100.4 (C-1'), 113.6 (CH), 128.1 (CH), 128.3 (CH), 128.3 (CH), 128.4 (CH), 128.8 (C), 129.0 (C), 129.2 (C), 129.3 (C), 129.5 (CH), 129.7 (CH), 129.8 (CH), 129.8 (CH), 129.9 (CH), 132.9 (CH), 133.0 (CH), 133.2 (CH), 159.2 (C), 164.7 (CO), 164.9 (CO), 165.2 (CO), 165.4 (CO), 166.1 (CO). Anal. Calcd for $C_{53}H_{46}O_{15}$ (·0,7 CH_3OH): C, 68.23; H, 5.20. Found: C, 68.23; H, 5.11.

4.4. 4-Methoxybenzyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→4)-2,3-di-*O*-benzoyl-α-L-arabinopyranoside (15). This compound was prepared using the general method described for **13.** Reaction of 4-methoxybenzyl 2,3-di-*O*-benzoyl-α-L-arabinopyranoside **11**[5] (0.5 g, 1.0 mmol) and trichloroacetimidate **12** (0.95 g, 1.6 mmol) gave 0.89 g (92%) of **15**. R_f = 0.46 (toluene/acetone 9:1). $[\alpha]_D$ = +9.0° (c 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 3.85 (s, 3H, OCH_3), 3.87 (m, 2H, H-5, H-5'), 4.39 (dd, 1H, J = 12.0, J = 6.1 Hz, H-5), 4.48 (m, 1H, H-4), 4.57 (dd, 1H, J = 12.5, J = 3.6 Hz, H-5'), 4.64 (d, 1H, J = 11.5 Hz, CH_2MPM), 4.85 (d, 1H, J = 4.8 Hz, H-1), 4.90 (d, 1H, J = 11.5 Hz, CH_2MPM), 5.14 (d, 1H, J = 4.2 Hz, H-1'), 5.31 (m, 1H, H-4'), 5.42 (dd, 1H, J = 6.0, J = 4.3 Hz, H-2'), 5.53 (dd, 1H, J = 7.1, J = 3.2 Hz, H-3), 5.66 (dd, 1H, J = 7.0, J = 4.9 Hz, H-2), 5.75 (t, 1H, J = 6.0 Hz, H-3'), 6.84 (d, 2H, J = 8.7 Hz, Ar-H), 7.14-7.62 (m, 17H, Ar-H), 7.82 (d, 2H, J = 8.3 Hz, Ar-H), 7.92 (d, 2H, J = 8.4 Hz, Ar-H), 8.02-8.07 (m, 6H, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 55.2 (OCH_3), 60.5 (C-5'), 62.3 (C-5), 68.4 (C-4'), 68.8 (C-3'), 69.5 (C-2'), 69.8 (CH_2MPM), 69.8 (C-2, C-3), 72.1 (C-4), 98.1 (C-1), 99.4 (C-1'), 113.7 (CH), 128.2 (CH), 128.4 (CH), 128.5 (CH), 128.9 (C), 129.0 (C), 129.1 (C), 129.1 (C), 129.2 (C), 129.4 (C), 129.7 (CH), 129.8 (CH), 129.9 (CH), 129.9 (CH), 133.0 (CH), 133.0 (CH), 133.2 (CH), 133.3 (CH), 133.3 (CH), 159.2 (C), 164.8 (CO), 165.2 (CO), 165.5 (CO), 165.7 (CO). Anal. Calcd for $C_{53}H_{46}O_{15}$: C, 68.97; H, 5.02. Found: C, 68.74; H, 4.71.

4.5. 3,4,6-Tri-*O*-acetyl-1,2-*O*-(1-ethylthioethylidene)-α-D-glucopyranose (19). A solution of HBr in AcOH (33%, 38 mL) was slowly added to a stirring solution of 1,2,3,4,6-penta-*O*-acetyl-D-glucopyranose (10.5 g, 26.9 mmol) in CH_2Cl_2 (38 mL) at 0 °C. After stirring overnight at room temperature the reaction mixture was diluted with CH_2Cl_2, washed with H_2O (200 mL), $NaHCO_3$ (sat.) (2 × 200 mL), NaCl (sat.) and dried with Na_2SO_4. The solvent was evaporated and the residue (11 g) was taken up in nitromethane (27 mL). After addition of 2,6-lutidine (4.7 mL, 40.4 mmol, 1.5 eq), ethanethiol (8.0 mL, 107.6 mmol, 4 eq) and tetrabutylammonium bromide (0.87 g, 2.7 mmol, 0.1 eq), the reaction was stirred at room temperature for 48h. The solution was then partitioned between EtOAc and aq. $NaHCO_3$. The aqueous layer was extracted with EtOAc, dried (Na_2SO_4), filtered and evaporated. The residue was purified by column chromatography (cyclohexane/EtOAc 8:2 to 7:3) to give 9.2 g (83%) of **19** as an oil. ^{1}H and ^{13}C NMR spectra were performed in deuterated chloroform and were in accordance with published data.[27]

4.6. 3,4,6-Tri-*O*-benzyl-1,2-*O*-(1-ethylthioethylidene)-α-D-glucopyranose (20). To a solution of orthoester **19** (8.9 g, 22.7 mmol) and benzyl bromide (8.7 mL, 72.6 mmol, 3.2 eq) in dry THF (55 mL) was added powdered KOH (14 g, 250 mmol, 11 eq) and the reaction was refluxed overnight with stirring. After the mixture was cooled, EtOAc was added, and the solution was successively washed with H_2O (3×), $NaHCO_3$ (sat) (2×), and H_2O (2×). The organic layer was dried (Na_2SO_4), evaporated, and the crude residue was purified by column chromatography (cyclohexane/EtOAc 97:3) to give 6.8 g (55%) of **20** as an oil. $[\alpha]_D$ = +17.1° (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 1.34 (t, 3H, *J* = 7.5 Hz, SCH_2CH_3), 1.99 (s, 3H, C*H*$_3$ orthoester), 2.69 (q, 2H, *J* = 7.5 Hz, SC*H*$_2$CH$_3$), 3.69 (dd, 1H, *J* = 10.9, *J* = 4.2 Hz, H-6a), 3.73 (dd, 1H, *J* = 10.9, *J* = 1.9 Hz, H-6b), 3.79 (dd, 1H, *J* = 9.5, *J* = 3.1 Hz, H-4), 3.89 (m, 1H, H-5), 3.99 (t, 1H, *J* = 3.0 Hz, H-3), 4.41 (d, 1H, *J* = 11.5 Hz, C*H*$_2$Ph), 4.58 (d, 1H, *J* = 12.2 Hz, C*H*$_2$Ph), 4.60 (d, 1H, *J* = 11.5 Hz, C*H*$_2$Ph), 4.63 (m, 1H, H-2), 4.64 (d, 1H, *J* = 11.9 Hz, C*H*$_2$Ph), 4.65 (d, 1H, *J* = 11.2 Hz, C*H*$_2$Ph), 4.75 (d, 1H, *J* = 11.9 Hz, C*H*$_2$Ph), 5.85 (d, 1H, *J* = 5.3 Hz, H-1), 7.24-7.43 (m, 15H, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 15.2 (SCH$_2$*C*H$_3$), 24.8 (S*C*H$_2$CH$_3$), 27.8 (*C*H$_3$ orthoester), 69.1 (C-6), 70.1 (C-5), 71.7 (*C*H$_2$Ph), 72.5 (*C*H$_2$Ph), 73.4 (*C*H$_2$Ph), 74.5 (C-2), 75.1 (C-4), 77.4 (C-3), 98.2 (C-1), 115.7 (C orthoester), 127.6 (CH), 127.8 (CH), 127.9 (CH), 128.0 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 137.6 (C), 137.8 (C), 138.1 (C). Anal. Calcd for $C_{31}H_{36}O_6S$: C, 69.38; H, 6.76. Found: C, 69.50; H, 6.88.

4.7. Ethyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (21). To a solution of orthoester **20** (6.6 g, 12.3 mmol) in CH_2Cl_2 (26 mL) was added 4 Å molecular sieves (1.6 g), and the mixture was stirred for 1h. The solution was cooled to 0 °C, and TMSOTf (0.11 mL, mmol, 0.05eq) was slowly added. After stirring for 4h, the reaction was quenched by the addition of Et_3N, filtered through celite and evaporated to dryness to give 6.4 g of a crude product which was used without further purification in the next step. For identification purposes, a small amount of product was purified by column chromatography (cyclohexane/EtOAc 95:5). $[\alpha]_D$ = +8.6° (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 1.33 (t, 3H, *J* = 7.4 Hz, SCH$_2$C*H*$_3$), 2.05 (s, 3H, C*H*$_3$CO), 2.78 (m, 2H, SC*H*$_2$CH$_3$), 3.57 (m, 1H, H-5), 3.74 (t, 1H, *J* = 9.0 Hz, H-3), 3.77 (t, 1H, *J* = 8.8 Hz, H-4), 3.78 (dd, 1H, *J* = 11.3, *J* = 4.5 Hz, H-6a), 3.83 (dd, 1H, *J* = 11.1, *J* = 1.9 Hz, H-6b), 4.43 (d, 1H, *J* = 10.0 Hz, H-1), 4.62 (d, 1H, J = 12.2 Hz, CH_2Ph), 4.64 (d, 1H, J = 11.0 Hz, CH_2Ph), 4.68 (d, 1H, J = 12.1 Hz, CH_2Ph), 4.76 (d, 1H, J = 11.4 Hz, CH_2Ph), 4.86 (d, 1H, J = 10.6 Hz, CH_2Ph), 4.88 (d, 1H, J = 11.3 Hz, CH_2Ph), 5.10 (t, 1H, J = 9.2 Hz, H-2), 7.26-7.41 (m, 15H, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 14.9 (SCH_2*C*H_3), 21.0 (*C*H_3CO), 23.8 (S*C*H_2CH_3), 68.8 (C-6), 71.7 (C-2), 73.4 (*C*H_2Ph), 75.1 (*C*H_2Ph), 75.2 (*C*H_2Ph), 77.8 (C-4), 79.4 (C-5), 83.4 (C-1), 84.4 (C-3), 127.6 (CH), 127.8 (CH), 127.9 (CH), 128.0 (CH), 128.3 (CH), 128.4 (CH), 137.9 (C), 138.1 (C), 138.2 (C), 169.6 (CO). Anal. Calcd for $C_{31}H_{36}O_6S$: C, 69.38; H, 6.76. Found: C, 69.23; H, 6.88.

4.8. Ethyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (22). The crude acetate **21** (6.3 g) was dissolved in a solution of 3% KOH /MeOH (80 mL) and was stirred overnight. The reaction mixture was then diluted with EtOAc, washed with H_2O (2×), dried (Na_2SO_4), filtered and evaporated. The crude product was taken up in pyridine (35 mL) and the reaction was cooled to 0 °C. Benzoyl chloride (2.8 mL, 24.6 mmol, 2 eq) was added dropwise, and after warming to room temperature, the reaction was heated to 70 °C for 6 h. The solvent was then removed under reduced pressure and the residue dissolved in EtOAc. The organic layer was washed with H_2O, 1N HCl, $NaHCO_3$ (sat.), and dried (Na_2SO_4). After filtration and evaporation of the solvent under reduced pressure the crude product was purified by column chromatography (cyclohexane/EtOAc 92:8) to give 3.45 g (49%) of benzoate **22** as an amorphous solid. $[\alpha]_D$ = +28.3° (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 1.31 (t, 3H, J = 7.4, SCH_2CH_3), 2.79 (m, 2H, S$CH_2$$CH_3$), 3.64 (m, 1H, H-5), 3.81 (dd, 1H, J = 11.0, J = 4.7, H-6a), 3.83 (t, 1H, J = 8.8, H-4), 3.86 (dd, 1H, J = 10.8, J = 1.7, H-6b), 3.91 (t, 1H, J = 9.0, H-3), 4.60 (d, 1H, J = 10.0, H-1), 4.64 (d, 1H, J = 12.1, CH_2Ph), 4.67 (d, 1H, J = 11.5, CH_2Ph), 4.69 (d, 1H, J = 12.5, CH_2Ph), 4.73 (d, 1H, J = 11.1, CH_2Ph), 4.81 (d, 1H, J = 11.1, CH_2Ph), 4.89 (d, 1H, J = 10.9, CH_2Ph), 5.38 (t, 1H, J = 9.6, H-2), 7.26-8.10 (m, 20H, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 14.9 (SCH_2*C*H_3), 23.8 (S*C*H_2CH_3), 68.9 (C-6), 72.4 (C-2), 73.5 (*C*H_2Ph), 75.1 (*C*H_2Ph), 75.3 (*C*H_2Ph), 77.9 (C-4), 79.5 (C-5), 83.4 (C-1), 84.3 (C-3), 127.6 (CH), 127.7 (CH), 127.8 (CH), 128.0 (CH), 128.2 (CH), 128.4 (CH), 129.8 (CH), 129.9 (C), 133.1 (CH), 137.7 (C), 137.9 (C), 138.1 (C), 165.3 (CO). Anal. Calcd for $C_{36}H_{38}O_6S$: C, 72.02; H, 6.4. Found: C, 72.02; H, 6.31.

4.9. 4-Methoxybenzyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-arabinopyranoside (23). General Method. In a typical experiment, a mixture of alcohol **9** (3.0 g, 6.3 mmol), thioglycoside **22** (5.63 g, 9.4 mmol, 1.5 eq), and 4 Å powdered molecular sieves (15 g) was stirred for 2 h at room temperature in CH_2Cl_2 (72 mL). The mixture was cooled to 0 °C and *N*-iodosuccinimide (2.12 g, 9.4 mmol, 1.5 eq) was added followed by the dropwise addition of triflic acid (0.028 mL, 0.05 eq). After 2 h at 0°C, the reaction was quenched with triethylamine and filtered through Celite. The filtrate was washed with $NaHCO_3$, 10% $Na_2S_2O_3$, and water. The organic layer was dried (Na_2SO_4), filtered and evaporated. The crude residue was purified by column chromatography (toluene/acetone 99:1) to give 5.22 g (82%) of disaccharide **23** as a white amorphous solid. R_f = 0.58 (toluene/acetone 9:1). $[\alpha]_D$ = +33.4° (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 3.63 (m, 1H, H-5'), 3.82 (m, 4H, H-6'a/b, H-3', H-5a), 3.84 (s, 3H, OCH_3), 3.86 (t, 1H, *J* = 9.5 Hz, H-4'), 4.17 (dd, 1H, *J* = 11.3, *J* = 8.0 Hz, H-5b), 4.26 (m, 1H, H-2), 4.54 (d, 1H, *J* = 11.1 Hz, CH_2MPM), 4.61 (d, 1H, *J* = 12.1 Hz, CH_2Ph), 4.64 (m, 3H, CH_2Ph), 4.75 (d, 1H, *J* = 11.0 Hz, CH_2Ph), 4.83 (d, 1H, *J* = 11.1 Hz, CH_2MPM), 4.87 (d, 1H, *J* = 10.9 Hz, CH_2Ph), 4.90 (d, 1H, *J* = 7.9 Hz, H-1'), 4.96 (d, 1H, *J* = 2.6 Hz, H-1), 5.32 (m, 1H, H-4), 5.38 (t, 1H, *J* = 8.3 Hz, H-2'), 5.46 (m, 1H, H-3), 6.87 (d, 2H, *J* = 8.2 Hz, Ar-H), 7.26-7.67 (m, 26H, Ar-H), 7.85 (d, 2H, *J* = 7.9 Hz, Ar-H), 7.90 (d, 2H, *J* = 7.9 Hz, Ar-H), 7.96 (d, 2H, *J* = 7.8 Hz, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 55.3 (OCH_3), 58.8 (C-5), 66.8 (C-4), 68.7 (C-6'), 69.7 (C-3), 69.8 (CH_2MPM), 73.4 (C-2'), 73.6 (CH_2Ph), 74.9 (C-2), 75.0 (2 × CH_2Ph), 75.5 (C-5'), 77.8 (C-4'), 82.6 (C-3'), 98.9 (C-1), 100.9 (C-1'), 113.7 (CH), 127.6 (CH), 127.6 (CH), 127.8 (CH), 127.8 (CH), 128.0 (CH), 128.0 (CH), 128.3 (CH), 128.3 (CH), 128.4 (CH), 129.5 (C), 129.6 (C), 129.7 (CH), 129.7 (CH), 132.9 (CH), 133.0 (CH), 133.1 (CH), 137.6 (C), 137.9 (C), 138.2 (C), 159.4 (C), 164.9 (CO), 165.1 (CO), 165.6 (CO). Anal. Calcd for $C_{61}H_{58}O_{14}$: C, 72.18; H, 5.76. Found: C, 71.91; H, 5.89.

4.10. 4-Methoxybenzyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-arabinopyranoside (24). This compound was prepared using the general method described for **23.** Reaction of 4-methoxybenzyl 2,4-di-*O*-benzoyl-α-L-arabinopyranoside **10**[5] (0.96 g, 2.0 mmol) and thioglycoside **22** (1.8 g, 3.0 mmol) gave 1.06 g (52%) of **24**. R_f = 0.52 (toluene/acetone 9:1). $[\alpha]_D$ = +45.4° (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 3.57 (m, 1H, H-5'), 3.64 (dd, 1H, *J* = 12.6, *J* = 2.2 Hz, H-5a), 3.66 (m, 2H, H-6'a/b), 3.73 (t, 1H, *J* = 8.8 Hz, H-4'), 3.76 (t, 1H, *J* = 8.7 Hz, H-3'), 3.79 (s, 3H, OCH_3), 4.24 (dd, 1H, *J* = 7.9, *J* = 3.5 Hz, H-3), 4.31 (dd, 1H, *J* = 12.6, *J* = 4.7 Hz, H-5b), 4.39 (d, 1H, *J* = 12.0 Hz, CH_2Ph), 4.42 (d, 1H, *J* = 11.9 Hz, CH_2Ph), 4.45 (d, 1H, *J* = 12.4 Hz, CH_2MPM), 4.50 (d, 1H, *J* = 5.9 Hz, H-1), 4.55 (m, 2H, CH_2Ph, CH_2MPM), 4.58 (d, 1H, *J* = 11.1 Hz, CH_2Ph), 4.66 (d, 1H, *J* = 11.1 Hz, CH_2Ph), 4.77 (d, 1H, *J* = 10.9 Hz, CH_2Ph), 4.80 (d, 1H, *J* = 7.7 Hz, H-1'), 5.28 (t, 1H, *J* = 8.2 Hz, H-2'), 5.50 (m, 2H, H-2, H-4), 6.69 (d, 2H, *J* = 8.7 Hz, Ar-H), 6.97 (d, 2H, *J* = 8.6 Hz, Ar-H), 7.07-7.60 (m, 24H, Ar-H), 7.83 (d, 2H, *J* = 7.6 Hz, Ar-H), 7.86 (d, 2H, *J* = 7.3 Hz, Ar-H), 8.16 (dd, 2H, *J* = 8.4, *J* = 1.2 Hz, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 55.1 (OCH_3), 61.9 (C-5), 68.9 (CH_2MPM), 70.0 (C-4), 71.2 (C-2), 73.4 (CH_2Ph), 73.4 (C-2'), 74.8 (CH_2Ph), 74.9 (CH_2Ph), 75.2 (C-5', C-3), 77.7 (C-4'), 82.7 (C-3'), 98.1 (C-1), 101.1 (C-1'), 113.6 (CH), 127.5 (CH), 127.6 (CH), 127.8 (CH), 127.8 (CH), 128.0 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 128.3 (CH), 128.4 (CH), 128.8 (C), 129.6 (CH), 129.7 (CH), 129.8 (C), 130.1 (CH), 132.6 (CH), 133.0 (CH), 137.7 (C), 137.9 (C), 138.2 (C), 159.1 (C), 164.7 (CO), 166.3 (CO). Anal. Calcd for $C_{61}H_{58}O_{14}$: C, 72.18; H, 5.76. Found: C, 71.95; H, 5.86.

4.11. 4-Methoxybenzyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzoyl-α-L-arabinopyranoside (25). This compound was prepared using the general method described for **23.** Reaction of 4-methoxybenzyl 2,3-di-*O*-benzoyl-α-L-arabinopyranoside **11**[5] (0.5 g, 1.0 mmol) and thioglycoside **22** (0.94 g, 1.6 mmol) gave 0.87 g (82%) of **25**. R_f = 0.56 (toluene/acetone 9:1). $[\alpha]_D$ = +7.2° (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 3.61 (m, 1H, H-5'), 3.77 (m, 2H, H-6'a/b), 3.82 (m, 2H, H-3', H-4'), 3.84 (s, 3H, OCH_3), 3.86 (m, 1H, H-5a), 4.35 (dd, 1H, *J* = 11.4, *J* = 8.3 Hz, H-5b), 4.47 (m, 1H, H-4), 4.53 (d, 1H, *J* = 11.3 Hz, CH_2MPM), 4.62 (d, 2H, *J* = 12.2 Hz, CH_2Ph), 4.65 (d, 1H, *J* = 12.8 Hz, CH_2Ph), 4.69 (d, 1H, *J* = 12.2 Hz, CH_2Ph), 4.72 (d, 1H, *J* = 11.0 Hz, CH_2Ph), 4.80 (d, 1H, *J* = 11.4 Hz, CH_2MPM), 4.81 (d, 1H, *J* = 7.7 Hz, H-1'), 4.85 (m, 2H, H-1, CH_2Ph), 5.32 (t, 1H, *J* = 8.2 Hz, H-2'), 5.45 (dd, 1H, *J* = 5.3, *J* = 3.0 Hz, H-2), 5.47 (dd, 1H, *J* = 5.4, *J* = 2.9 Hz, H-3), 6.82 (d, 2H, *J* = 8.6 Hz, Ar-H), 7.10-7.60 (m, 26H, Ar-H), 7.67 (d, 2H, *J* = 7.2 Hz, Ar-H), 7.87 (d, 2H, *J* = 7.3 Hz, Ar-H), 8.30 (d, 2H, *J* = 7.2 Hz, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 55.2 (OCH_3), 60.9 (C-5), 68.6 (C-6'), 69.0 (C-2), 69.3 (CH_2MPM), 69.7 (C-3), 70.7 (C-4), 73.4 (CH_2Ph, C-2'), 74.9 (CH_2Ph), 75.0 (CH_2Ph), 75.2 (C-5'), 77.8 (C-4'), 82.7 (C-3'), 97.0 (C-1), 100.0 (C-1'), 113.7 (CH), 127.6 (CH), 127.7 (CH), 127.7 (CH), 127.8 (CH), 128.0 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 128.4 (CH), 128.4 (CH), 129.1 (C), 129.3 (C), 129.4 (C), 129.6 (CH), 129.7 (CH), 129.8 (CH), 129.8 (CH), 159.2 (C), 164.7 (CO), 164.9 (CO), 165.4 (CO). Anal. Calcd for $C_{61}H_{58}O_{14}$: C, 72.18; H, 5.76. Found: C, 72.07; H, 5.80.

4.12. 2,3,4-Tri-*O*-benzoyl-β-D-xylopyranosyl-(1→2)-3,4-di-*O*-benzoyl-β-L-arabinopyranosyl trichloroacetimidate (27). General method. In a typical experiment, trifluoroacetic acid (4.0 mL, 52.5 mmol, 20 eq) and H_20 (0.56 mL, 31.6 mmol, 12 eq) were added to a solution of the disaccharide **13** (2.42 g, 2.6 mmol) in CH_2Cl_2 (90 mL). The reaction was vigorously stirred overnight before being washed with H_2O, $NaHCO_3$ (sat.), and NaCl (sat.). The dried solution (Na_2SO_4) was then evaporated under reduced pressure and the residue taken up in CH_2Cl_2 (30 mL). Trichloroacetonitrile (1.3 mL, 12.8 mmol, 5 eq) was added, followed by DBU (0.04 mL, 0.26 mmol, 0.1 eq), and the reaction was stirred overnight. The reaction was then evaporated and the crude residue was purified by column chromatography (cyclohexane/EtOAc/Et_3N 9:1:0.1) to give 2.20 g (89%) of **27** as a white amorphous solid. R_f = 0.53 (cyclohexane/EtOAc 6:4). $[\alpha]_D$ = +94.6° (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 3.81 (dd, 1H, *J* = 12.3, *J* = 6.7 Hz, H-5'), 4.09 (dd, 1H, *J* = 13.2, *J* = 1.6 Hz, H-5), 4.37 (brd, 1H, *J* = 12.9 Hz, H-5), 4.54 (dd, 1H, *J* = 12.4, *J* = 4.4 Hz, H-5'), 4.62 (dd, 1H, *J* = 10.4, *J* = 3.6 Hz, H-2), 5.17 (d, 1H, *J* = 5.4 Hz, H-1'), 5.34 (m, 1H, H-4'), 5.37 (dd, 1H,

J = 7.8, J = 5.5 Hz, H-2'), 5.71 (t, 1H, J = 7.5 Hz, H-3'), 5.77 (dd, 1H, J = 10.4, J = 3.5 Hz, H-3), 5.82 (m, 1H, H-4), 6.79 (d, 1H, J = 3.5 Hz, H-1), 7.12 (t, 2H, J = 7.7 Hz, Ar-H), 7.30-7.67 (m, 15H, Ar-H), 7.80 (d, 2H, J = 8.3 Hz, Ar-H), 7.91 (d, 2H, J = 8.4 Hz, Ar-H), 8.04 (d, 2H, J = 8.4 Hz, Ar-H), 8.08 (d, 2H, J = 8.4 Hz, Ar-H), 8.82 (s, 1H, N*H*). ^{13}C NMR ($CDCl_3$) : δ 61.7 (C-5'), 62.8 (C-5), 69.3 (C-3), 69.4 (C-4'), 69.5 (C-4), 70.2 (C-2'), 70.2 (C-3'), 74.0 (C-2), 95.9 (C-1), 101.7 (C-1'), 128.1 (CH), 128.3 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 128.8 (C), 120.0 (C), 129.1 (C), 129.5 (CH), 129.5 (CH), 129.5 (C), 129.8 (CH), 129.9 (CH), 132.9 (C), 133.1 (C), 133.3 (C), 133.4 (C), 161.1 (*C*=NH), 164.7 (CO), 165.1 (CO), 165.4 (CO), 165.5 (CO). Anal. Calcd for $C_{47}H_{38}Cl_3NO_{14}$: C, 59.60; H, 4.04; N, 1.48. Found: C, 59.45; H, 4.07; N, 1.40.

4.13. 2,3,4-Tri-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-β-L-arabinopyranosyl trichloroacetimidate (28). This compound was prepared using the general method described for **27.** Deprotection of disaccharide **14** (0.65 g, 0.7 mmol) followed by trichloroacetimidate formation gave 0.53 g (80%) of **28**. R_f = 0.55 (cyclohexane/EtOAc 6:4). $[\alpha]_D$ = +45.6° (*c* 0.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 3.81 (dd, 1H, J = 12.5, J = 5.7 Hz, H-5'), 4.20 (dd, 1H, J = 13.4, J = 2.0 Hz, H-5), 4.31 (brd, 1H, J = 12.9 Hz, H-5), 4.47 (dd, 1H, J = 12.6, J = 4.0 Hz, H-5'), 4.68 (dd, 1H, J = 10.3, J = 3.4 Hz, H-3), 5.26 (m, 2H, H-1', H-4'), 5.34 (dd, 1H, J = 7.0, J = 4.8 Hz, H-2'), 5.67 (t, 1H, J = 6.8 Hz, H-3'), 5.78 (m, 1H, H-4), 5.85 (dd, 1H, J = 10.3, J = 3.6 Hz, H-2), 6.74 (d, 1H, J = 3.6 Hz, H-1), 7.17 (t, 2H, J = 7.6 Hz, Ar-H), 7.27 (t, 2H, J = 7.6 Hz, Ar-H), 7.35 (t, 2H, J = 7.7 Hz, Ar-H), 7.40-7.69 (m, 11H, Ar-H), 7.87 (d, 2H, J = 8.3 Hz, Ar-H), 7.92 (d, 2H, J = 8.4 Hz, Ar-H), 8.04 (d, 2H, J = 8.4 Hz, Ar-H), 8.17 (d, 2H, J = 8.4 Hz, Ar-H), 8,60 (s, 1H, N*H*). ^{13}C NMR ($CDCl_3$) : δ 61.2 (C-5'), 63.1 (C-5), 69.0 (C-4'), 69.5 (C-2), 69.7 (C-3'), 69.9 (C-2'), 71.4 (C-4), 73.5 (C-3), 94.3 (C-1-), 101.4 (C-1'), 128.1 (CH), 128.3 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 128.8 (C), 128.8 (C), 129.2 (C), 129.5 (CH), 129.5 (C), 129.6 (CH), 129.6 (CH), 129.9 (CH), 130.0 (CH), 132.9 (CH), 133.2 (CH), 133.3 (CH), 133.3 (CH), 133.4 (CH), 160.5 (*C*=NH), 164.6 (CO), 165.2 (CO), 165.3 (CO), 165.4 (CO), 166.1 (CO). Anal. Calcd for $C_{47}H_{38}Cl_3NO_{14}$: C, 59.60; H, 4.04; N, 1.48. Found: C, 59.25; H, 3.93; N, 1.35.

4.14. 2,3,4-Tri-*O*-benzoyl-β-D-xylopyranosyl-(1→4)-2,3-di-*O*-benzoyl-β-L-arabinopyranosyl trichloroacetimidate (29). This compound was prepared using the general method described for **27.** Deprotection of disaccharide **15** (0.65 g, 0.7 mmol) followed by trichloroacetimidate formation gave 0.56 g (83%) of **29**. R_f = 0.55 (cyclohexane/EtOAc 6:4). $[\alpha]_D$ = +50.1° (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 3.86 (dd, 1H, J = 12.5, J = 5.1 Hz, H-5'), 4.28 (dd, 1H, J = 12.7, J = 1.5 Hz, H-5), 4.37 (brd, 1H, J = 12.7 Hz, H-5), 4.59 (m, 2H, H-4, H-5'), 5.13 (d, 1H, J = 3.8 Hz, H-1'), 5.34 (m, 1H, H-4'), 5.54 (dd, 1H, J = 5.5, J = 4.1 Hz, H-2'), 5.77 (t, 1H, J = 5.7 Hz, H-3'), 5.87 (dd, 1H, J = 10.7,

J = 3.4 Hz, H-2), 5.93 (dd, 1H, J = 10.7, J = 2.9 Hz, H-3), 6.86 (d, 1H, J = 3.3 Hz, H-1), 7.24-7.62 (m, 15H, Ar-H), 7.90 (d, 2H, J = 7.4 Hz, Ar-H), 7.94 (d, 2H, J = 7.4 Hz, Ar-H), 7.96 (d, 2H, J = 7.4 Hz, Ar-H), 8.04 (d, 2H, J = 7.4 Hz, Ar-H), 8.18 (d, 2H, J = 7.4 Hz, Ar-H), 8.66 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) : δ 60.4 (C-5’), 64.6 (C-5), 68.1 (C-2), 68.2 (C-4’), 68.5 (C-3’), 69.4 (C-2’, C-3), 74.8 (C-4), 94.2 (C-1), 100.5 (C-1’), 128.2 (CH), 128.3 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 128.7 (C), 128.9 (C), 129.0 (C), 129.1 (C), 129.2 (C), 129.7 (CH), 129.7 (CH), 129.8 (CH), 130.0 (CH), 133.1 (CH), 133.2 (CH), 133.3 (CH), 133.5 (CH), 160.8 (C=NH), 164.9 (CO), 165.1 (CO), 165.2 (CO), 165.4 (CO), 165.9 (CO). Anal. Calcd for $C_{47}H_{38}Cl_3NO_{14}$: C, 59.60; H, 4.04; N, 1.48. Found: C, 59.23; H, 4.04; N, 1.58.

4.15. 2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzoyl-β-L-arabinopyranosyl trichloroacetimidate (30). This compound was prepared using the general method described for **27.** Deprotection of disaccharide **23** (6.47g, 6.4 mmol) followed by trichloroacetimidate formation gave 4.6 g (78%) of **30**. R_f = 0.64 (cyclohexane/ EtOAc 6:4). $[\alpha]_D$ = +110.7° (c 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 3.68 (m, 1H, H-5’), 3.77 (t, 1H, J = 9.1 Hz, H-3’), 3.84 (t, 1H, J = 9.4 Hz, H-4’), 3.87 (m, 2H, H-6’a/b), 4.07 (dd, 1H, J = 13.3, J = 1.8 Hz, H-5a), 4.31 (d, 1H, J = 12.9 Hz, H-5b), 4.56 (m, 1H, H-2), 4.57 (d, 1H, J = 11.3 Hz, CH_2Ph), 4.66 (m, 3H, CH_2Ph), 4.71 (d, 1H, J = 11.9 Hz, CH_2Ph), 4.84 (d, 1H, J = 10.8 Hz, CH_2Ph), 4.87 (d, 1H, J = 7.8 Hz, H-1’), 5.25 (dd, 1H, J = 9.2, J = 7.9 Hz, H-2’), 5.68 (dd, 1H, J = 10.4, J = 3.5 Hz, H-3), 3.78 (m, 1H, H-4), 6.79 (d, 1H, J = 3.6 Hz, H-1), 7.07-7.65 (m, 25H, Ar-H), 7.74 (dd, 2H, J = 8.3, J = 1.2 Hz, Ar-H), 8.05 (dd, 2H, J = 8.3, J = 1.3 Hz, Ar-H), 8.11 (dd, 1H, J = 8.3, J = 1.3 Hz, Ar-H), 8.64 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) : δ 62.7 (C-5), 68.9 (C-6’), 69.4 (C-4), 69.7 (C-3), 73.0 (C-2), 73.4 (C-2’), 73.7 (CH$_2$Ph), 75.0 (CH$_2$Ph), 75.1 (CH$_2$Ph), 75.4 (C-5’), 77.7 (C-4’), 82.5 (C-3’), 96.2 (C-1), 101.6 (C-1’), 127.6 (CH), 127.7 (CH), 127.7 (CH), 127.9 (CH), 128.0 (CH), 128.2 (CH), 128.2 (CH), 128.4 (CH), 128.5 (CH), 129.1 (C), 129.2 (CH), 129.3 (C), 129.5 (CH), 129.6 (CH), 129.6 (C), 129.8 (CH), 132.6 (CH), 132.9 (CH), 133.0 (CH), 133.4 (CH), 137.6 (C), 137.9 (C), 138.1 (C), 161.2 (C=NH), 164.6 (CO), 164.9 (CO), 165.5 (CO). Anal. Calcd for $C_{55}H_{50}Cl_3NO_{13}$: C, 63.56; H, 4.85; N, 1.35. Found: C, 63.80; H, 4.59; N, 1.30.

4.16. 2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→3)-2,4-di-*O*-benzoyl-β-L-arabinopyranosyl trichloroacetimidate (31). This compound was prepared using the general method described for **27.** Deprotection of disaccharide **24** (0.97 g, 1.0 mmol) followed by trichloroacetimidate formation gave 0.66 g (74%) of **31**. R_f = 0.65 (cyclohexane/ EtOAc 6:4). $[\alpha]_D$ = +68.5° (c 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 3.66 (m, 1H, H-5’), 3.77 (m, 4H, H-3’, H-4’, H-6’a, H-6’b), 4.20 (m, 2H, H-5a, H-5b), 4.51 (d, 1H, J = 11.9, CH_2Ph), 4.56 (d, 3H, J = 11.5, CH_2Ph), 4.60

(dd, 1H, *J* = 10.2, *J* = 3.5, H-3), 4.65 (d, 1H, *J* = 11.1, C*H*$_2$Ph), 4.77 (d, 1H, *J* = 10.8, C*H*$_2$Ph), 4.93 (d, 1H, *J* = 7.6, H-1'), 5.24 (m, 1H, H-2'), 5.73 (m, 1H, H-4), 5.75 (dd, 1H, *J* =10.2, *J* = 3.5, H-2), 6.65 (d, 1H, *J* = 3.6, H-1), 7.06-7.62 (m, 24H, Ar-H), 7.66 (dd, 2H, *J* = 8.3, *J* = 1.3, Ar-H), 7.84 (dd, 2H, *J* = 8.4, *J* = 1.2, Ar-H), 8.15 (dd, 2H, *J* = 8.4, *J* = 1.4, Ar-H), 8.52 (s, 1H, N*H*). ^{13}C NMR ($CDCl_3$) : δ 62.9 (C-5), 68.9 (C-6'), 69.6 (C-2), 71.4 (C-4), 73.0 (C-3), 73.4 (C-2'), 73.5 (*C*H$_2$Ph), 74.7 (*C*H$_2$Ph), 75.0 (*C*H$_2$Ph), 75.3 (C-5'), 77.6 (C-4'), 82.5 (C-3'), 94.2 (C-1), 101.5 (C-1'), 127.5 (CH), 127.5 (CH), 127.7 (CH), 127.8 (CH), 128.0 (CH), 128.1 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 128.4 (CH), 128.4 (CH), 128.9 (C), 129.3 (CH), 129.4 (C), 129.6 (CH), 129.9 (C), 130.0 (CH), 132.7 (CH), 132.9 (CH), 133.1 (CH), 137.6 (C), 137.8 (C), 138.1 (C), 160.5 (*C*=NH), 164.6 (CO), 165.1 (CO), 166.3 (CO). Anal. Calcd for $C_{55}H_{50}Cl_3NO_{13}$: C, 63.56; H, 4.85; N, 1.35. Found: C, 63.17; H, 4.56; N, 1.38.

4.17. 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzoyl-β-L-arabinopyranosyl trichloroacetimidate (32). This compound was prepared using the general method described for **27.** Deprotection of disaccharide **25** (0.65 g, 0.6 mmol) followed by trichloroacetimidate formation gave 0.52 g (77%) of **32**. R_f = 0.63 (cyclohexane/ EtOAc 6:4). $[\alpha]_D$ = +66.3° (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 3.54 (m, 1H, H-5'), 3.72 (m, 2H, H-6'a/b), 3.81 (m, 2H, H-3', H-4'), 4.24 (d, 1H, *J* = 12.5 Hz, H-5a), 4.32 (dd, 1H, *J* = 12.6, *J* = 1.7 Hz, H-5b), 4.54 (m, 1H, H-4), 4.62 (m, 3H, C*H*$_2$Ph), 4.70 (d, 1H, *J* = 11.0 Hz, C*H*$_2$Ph), 4.77 (d, 1H, *J* = 11.9 Hz, C*H*$_2$Ph), 4.79 (d, 1H, *J* = 7.9 Hz, H-1'), 4.85 (d, 1H, *J* = 10.9 Hz, C*H*$_2$Ph), 5.47 (m, 1H, H-2'), 5.78 (m, 2H, H-2, H-3), 6.79 (d, 1H, *J* = 1.7 Hz, H-1), 7.17-7.54 (m, 24H, Ar-H), 7.78 (d, 2H, *J* = 7.3 Hz, Ar-H), 7.91 (d, 2H, *J* = 7.3 Hz, Ar-H), 7.97 (d, 2H, *J* = 7.3 Hz, Ar-H), 8.60 (s, 1H, N*H*). ^{13}C NMR ($CDCl_3$) : δ 64.8 (C-5), 67.8 (C-2), 68.7 (C-6'), 69.9 (C-3), 73.5 (*C*H$_2$Ph), 73.7 (C-2'), 74.8 (C-4), 75.0 (2 × *C*H$_2$Ph), 75.1 (C-5'), 77.8 (C-4'), 82.8 (C-3'), 94.6 (C-1), 101.9 (C-1'), 127.6 (CH), 127.7 (CH), 127.9 (CH), 128.3 (CH), 128.5 (CH), 128.8 (C), 129.1 (C), 129.5 (CH), 129.7 (CH), 129.7 (CH), 129.8 (C), 132.7 (CH), 133.1 (CH), 133.2 (CH), 137.7 (C), 137.7 (C), 137.8 (C), 138.0 (C), 160.6 (*C*=NH), 164.9 (CO), 165.0 (CO), 166.0 (CO). Anal. Calcd for $C_{55}H_{50}Cl_3NO_{13}$: C, 63.56; H, 4.85; N, 1.35. Found: C, 63.88; H, 5.14; N, 1.26.

4.18. Allyl 3-*O*-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-arabinopyranosyl]-23-*O*-benzoylhederagenate (34). General coupling method. In a typical experiment, allyl hederagenate **33**[5] (0.150 g, 0.24 mmol), trichloroacetimidate **28** (0.35 g, 0.37 mmol, 1.5 eq) and 4 Å powdered molecular sieves (1 g) were stirred for 1h at room temperature in CH_2Cl_2 (4 mL). The mixture was cooled to –20 °C for 30 minutes followed by the dropwise addition of a 0.1 M solution of TMSOTf in CH_2Cl_2 (0.12 mL, 0.012 mmol, 0.05 eq). After 6h at -20

°C the reaction was quenched with triethylamine, filtered through Celite and evaporated. Purification by column chromatography (toluene/acetone 99:1 to 98.5:1.5) gave 0.32 g (95%) of saponin **34** as a white foam. R_f = 0.63 (toluene/acetone 9:1). $[\alpha]_D$ = +53.1° (*c* 1, $CHCl_3$). ^1H NMR ($CDCl_3$) : δ 0.63 (s, 3H, H-24), 0.73 (s, 3H, H-26), 0.90-1.98 (m, 22H, H-1, H-2, H-5, H-6, H-7, H-9, H-11, H-15, H-16, H-19, H-21, H-22), 0.93 (s, 3H, H-25), 0.94 (s, 3H, H-29), 0.96 (s, 3H, H-30), 1.05 (s, 3H, H-27), 2.91 (dd, 1H, *J* = 13.7, *J* = 3.8 Hz, H-18), 3.56 (dd, 1H, *J* = 11.6, *J* = 4.7 Hz, H-3), 3.66 (dd, 1H, *J* = 12.5, *J* = 5.7 Hz, H-5”), 3.69 (brd, 1H, *J* = 13.6 Hz, H-5’), 3.83 (d, 1H, *J* = 11.5 Hz, H-23), 4.09 (d, 1H, *J* = 11.6 Hz, H-23), 4.29 (m, 2H, H-3’, H-5’), 4.39 (dd, 1H, *J* = 12.5, *J* = 3.8 Hz, H-5”), 4.55 (m, 2H, $CH_2CH=CH_2$ with italic H: C*H*$_2$CH=CH$_2$), 4.65 (d, 1H, *J* = 7.1 Hz, H-1’), 5.14 (d, 1H, *J* = 4.5 Hz, H-1”), 5.19 (m, 1H, H-4”), 5.23 (dd, 1H, *J* = 10.8, *J* = 0.8 Hz, $CH_2CH=CH_2$), 5.27 (dd, 1H, *J* = 6.7, *J* = 4.7 Hz, H-2”), 5.34 (m, 2H, $CH_2CH=CH_2$, H-12), 5.55 (m, 1H, H-4’), 5.60 (t, 1H, *J* = 6.5 Hz, H-3”), 5.71 (dd, 1H, *J* = 8.9, *J* = 7.4 Hz, H-2’), 5.92 (m, 1H, $CH_2CH=CH_2$), 7.23 (t, 2H, *J* = 7.7 Hz, Ar-H), 7.30-7.65 (m, 16H, Ar-H), 7.70 (d, 2H, *J* = 7.6 Hz, Ar-H), 7.94 (d, 2H, *J* = 7.8 Hz, Ar-H), 7.96 (d, 2H, *J* = 7.6 Hz, Ar-H), 8.01 (d, 2H, *J* = 7.4 Hz, Ar-H), 8.04 (d, 2H, *J* = 7.3 Hz, Ar-H), 8.16 (d, 2H, *J* = 7.4 Hz, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 12.5 (C-24), 15.5 (C-25), 16.9 (C-26), 17.9 (C-6), 22.9 (C-16), 23.4 (C-11), 23.6 (C-30), 25.3 (C-27, C-2), 27.5 (C-15), 30.6 (C-20), 32.3 (C-7, C-22), 33.1 (C-29), 33.8 (C-21), 36.4 (C-10), 38.3 (C-1), 39.3 (C-8), 41.3 (C-18), 41.6 (C-14), 42.1 (C-4), 45.8 (C-19), 46.7 (C-17), 48.0 (C-9), 48.1 (C-5), 60.8 (C-5”), 63.2 (C-5’), 64.8 ($CH_2CH=CH_2$), 65.3 (C-23), 68.8 (C-4”), 69.5 (C-3”), 69.8 (C-2”), 71.0 (C-4’), 71.3 (C-2’), 77.1 (C-3’), 83.4 (C-3), 100.7 (C-1”), 103.2 (C-1’), 117.7 ($CH_2CH=CH_2$), 122.4 (C-12), 128.0 (CH), 128.3 (CH), 128.3 (CH), 128.4 (CH), 128.6 (CH), 128.9 (C), 129.0 (C), 129.2 (C), 129.2 (C), 129.4 (CH), 129.7 (CH), 129.7 (CH), 129.8 (CH), 129.8 (CH), 130.0 (CH), 130.4 (C), 132.5 ($CH_2CH=CH_2$), 132.8 (CH), 132.9 (CH), 133.0 (CH), 133.3 (CH), 143.6 (C-13), 164.6 (CO), 164.9 (CO), 165.2 (CO), 165.4 (CO), 165.8 (CO), 166.2 (CO), 177.3 (C-28). Anal. Calcd for $C_{85}H_{92}O_{18}$: C, 72.84; H, 6.62. Found: C, 72.77; H, 6.85.

4.19. Allyl 3-*O*-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→4)-2,3-di-*O*-benzoyl-α-L-arabinopyranosyl]-23-*O*-benzoylhederagenate (35). This compound was prepared using the general method described for **34.** Reaction of allyl hederagenate **33** (0.150 g, 0.24 mmol) and trichloroacetimidate **28** (0.35 g, 0.37 mmol) gave 0.178 g (94%) of **35**. R_f = 0.61 (toluene/acetone 9:1). $[\alpha]_D$ = +46.0° (*c* 1, $CHCl_3$). As ^1H and ^{13}C chemical shifts for the hederagenin aglycone are nearly identical to those indicated above, only selected NMR data is presented: ^1H NMR ($CDCl_3$) : δ 0.69 (s, 3H, H-24), 0.76 (s, 3H, H-26), 0.95 (s, 3H, H-29), 0.98 (s, 3H, H-30), 1.00 (s, 3H, H-25), 1.07 (s, 3H, H-27), 2.93 (dd, 1H, *J* = 13.6, *J* = 3.8 Hz, H-18), 3.68 (dd, 1H, *J* = 11.6, *J* = 4.5 Hz, H-3), 3.77 (brd, 1H, *J* = 11.0 Hz, H-5’), 3.82 (dd, 1H, *J* = 12.5, *J* = 5.2 Hz, H-5”), 4.02 (d, 1H, *J* = 11.4

Hz, H-23), 4.10 (d, 1H, J = 11.6 Hz, H-23), 4.34 (dd, 1H, J = 12.4, J = 4.5 Hz, H-5'), 4.44 (m, 1H, H-4'), 4.56 (m, 3H, H-5", CH_2CH=CH_2), 4.80 (d, 1H, J = 5.9 Hz, H-1'), 5.08 (d, 1H, J = 4.0 Hz, H-1"), 5.25 (brd, 1H, J = 10.5 Hz, CH_2CH=CH_2), 5.30 (m, 1H, H-4"), 5.36 (m, 2H, H-12, CH_2CH=CH_2), 5.42 (dd, 1H, J = 5.7, J = 4.2 Hz, H-2"), 5.45 (dd, 1H, J = 8.5, J = 3.2 Hz, H-3'), 5.72 (t, 1H, J = 5.7 Hz, H-3"), 5.73 (m, 1H, H-2'), 5.94 (m, 1H, CH_2CH=CH_2). ^{13}C NMR ($CDCl_3$) : δ 12.7 (C-24), 15.6 (C-25), 16.9 (C-26), 23.6 (C-30), 25.4 (C-27), 33.1 (C-29), 60.4 (C-5"), 63.5 (C-5'), 65.4 (C-23), 68.5 (C-4"), 68.9 (C-3"), 69.6 (C-2"), 70.0 (C-2'), 71.3 (C-3'), 73.1 (C-4'), 82.4 (C-3), 99.8 (C-1"), 102.3 (C-1'), 122.3 (C-12), 143.6 (C-13), 177.3 (C-28). Anal. Calcd for $C_{85}H_{92}O_{18}$: C, 72.84; H, 6.62. Found: C, 72.70; H, 6.70.

4.20. Allyl 3-*O*-[2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-arabinopyranosyl]-23-*O*-benzoylhederagenate (36). This compound was prepared using the general method described for **34.** Reaction of allyl hederagenate **33** (0.31 g, 0.51 mmol) and trichloroacetimidate **31** (0.79 g, 0.76 mmol) gave 0.71 g (93%) of **36**. R_f = 0.72 (toluene/acetone 9:1). $[\alpha]_D$ = +69.0° (*c* 1, $CHCl_3$). Selected NMR data: ^{1}H NMR ($CDCl_3$) : δ 0.55 (s, 3H, H-24), 0.72 (s, 3H, H-26), 0.91 (s, 3H, H-25), 0.94 (s, 3H, H-29), 0.97 (s, 3H, H-30), 1.04 (s, 3H, H-27), 2.91 (dd, 1H, J = 13.6, J = 3.8 Hz, H-18), 3.53 (dd, 1H, J = 11.6, J = 4.8 Hz, H-3), 3.58 (m, 1H, H-5''), 3.59 (dl, 1H, J = 12.7 Hz, H-5a'), 3.69 (m, 2H, H-3'', H-4''), 3.75 (m, 3H, H-23a, H-6a/b''), 3.96 (d, 1H, J = 11.5 Hz, H-23b), 4.19 (dd, 1H, J = 9.9, J = 3.7 Hz, H-3'), 4.28 (dd, 1H, J = 13.4, J = 1.8 Hz, H-5b'), 4.54 (m, 7H, H-1', CH_2Ph, CH_2CH=CH_2), 4.61 (d, 1H, J = 11.0 Hz, CH_2Ph), 4.78 (d, 1H, J = 10.8 Hz, CH_2Ph), 4.79 (d, 1H, J = 7.7 Hz, H-1''), 5.20 (m, 1H, H-2''), 5.23 (m, 1H, CH_2CH=CH_2), 5.32 (m, 1H, H-12), 5.34 (m, 1H, CH_2CH=CH_2), 5.51 (m, 1H, H-4'), 5.62 (dd, 1H, J = 9.8, J = 7.8 Hz, H-2'), 5.92 (m, 1H, CH_2CH=CH_2). ^{13}C NMR ($CDCl_3$) : δ 12.5 (C-24), 15.5 (C-25), 16.9 (C-26), 23.6 (C-30), 25.3 (C-27), 25.4 (C-2), 33.1 (C-29), 64.0 (C-5'), 65.3 (C-23), 69.0 (C-6''), 71.6 (C-4'), 71.7 (C-2'), 73.4 (C-2''), 75.1 (C-5''), 76.6 (C-3'), 77.6 (C-4''), 82.1 (C-3), 82.7 (C-3''), 101.4 (C-1''), 103.4 (C-1'), 122.4 (C-12), 143.6 (C-13), 177.3 (C-28). Anal. Calcd for $C_{93}H_{104}O_{17}$ (·0.9 CH_3OH): C, 74.07; H, 7.12. Found: C, 73.91; H, 7.12.

4.21. Allyl 3-*O*-[2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzoyl-α-L-arabinopyranosyl]-23-*O*-benzoylhederagenate (37). This compound was prepared using the general method described for **34.** Reaction of allyl hederagenate **33** (0.11 g, 0.18 mmol) and trichloroacetimidate **32** (0.28 g, 0.27 mmol) gave 0.25 g (95%) of **37**. R_f = 0.70 (toluene/acetone 9:1). $[\alpha]_D$ = +50.0° (*c* 1, $CHCl_3$). Selected NMR data: ^{1}H NMR ($CDCl_3$) : δ 0.58 (s, 3H, H-24), 0.75 (s, 3H, H-26), 0.95 (s, 3H, H-29), 0.96 (s, 3H, H-25), 0.98 (s, 3H, H-30), 1.05 (s, 3H, H-27), 2.93 (dd, 1H, J = 13.3, J = 3.1 Hz, H-18), 3.55 (m, 1H, H-5''), 3.63 (dd, 1H, J = 11.7, J = 4.5 Hz, H-

3), 3.74 (m, 2H, H-6a/b’’), 3.76 (m, 1H, H-5a’), 3.80 (m, 2H, H-3’’, H-4’’), 4.01 (d, 1H, *J* = 11.5 Hz, H-23a), 4.07 (d, 1H, *J* = 11.5 Hz, H-23b), 4.36 (dd, 1H, *J* = 11.8, *J* = 6.7 Hz, H-5b’), 4.45 (m, 1H, H-4’), 4.57 (m, 2H, $CH_2CH=CH_2$), 4.60 (d, 1H, *J* = 12.3 Hz, CH_2Ph), 4.62 (d, 1H, *J* = 10.9 Hz, CH_2Ph), 4.65 (d, 1H, *J* = 9.0 Hz, CH_2Ph), 4.67 (d, 1H, *J* = 12.0 Hz, CH_2Ph), 4.73 (d, 1H, *J* = 11.0 Hz, CH_2Ph), 4.80 (d, 1H, *J* = 7.5 Hz, H-1’’), 4.80 (m, 1H, H-1’), 4.85 (d, 1H, *J* = 10.9 Hz, CH_2Ph), 5.25 (m, 1H, $CH_2CH=CH_2$), 5.35 (m, 2H, H-12, H-2’’), 5.36 (m, 1H, $CH_2CH=CH_2$), 5.38 (m, 1H, H-3’), 5.53 (dd, 1H, *J* = 6.7, *J* = 4.4 Hz, H-2’), 5.95 (m, 1H, $CH_2CH=CH_2$). ^{13}C NMR ($CDCl_3$) : δ 12.6 (C-24), 15.6 (C-25), 16.9 (C-26), 23.6 (C-30), 25.2 (C-2), 25.4 (C-27), 33.1 (C-29), 62.0 (C-5’), 65.5 (C-23), 68.6 (C-6’’), 69.8 (C-2’, C-3’), 71.4 (C-4’), 73.5 (C-2’’), 75.2 (C-5’’), 77.7 (C-4’’), 82.2 (C-3), 82.7 (C-3’’), 100.2 (C-1’’), 101.0 (C-1’), 122.4 (C-12), 143.6 (C-13), 177.3 (C-28). Anal. Calcd for $C_{93}H_{104}O_{17}$: C, 74.78; H, 7.02. Found: C, 74.51; H, 7.29.

4.22. Allyl 3-*O*-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→2)-2,3-di-*O*-benzoyl-β-L-arabinopyranosyl]-23-*O*-benzoylhederagenate (38). This compound was prepared at 0 °C using the general method described for **34.** Reaction of allyl hederagenate **33** (0.26 g, 0.41 mmol) and trichloroacetimidate **27** (0.59 g, 0.62 mmol) gave 0.55 g (94%) of **38**. R_f = 0.62 (toluene/acetone 9:1). $[\alpha]_D$ = +81.9° (*c* 1, $CHCl_3$). Selected NMR data: ^{1}H NMR ($CDCl_3$) : δ 0.83 (s, 3H, H-26), 0.96 (s, 6H, H-24, H-29), 0.99 (s, 3H, H-30), 1.10 (s, 3H, H-25), 1.13 (s, 3H, H-27), 2.96 (dd, 1H, *J* = 14.2, *J* = 3.7 Hz, H-18), 3.72 (dd, 1H, *J* = 11.9, *J* = 8.3 Hz, H-5”), 3.82 (brd, 1H, *J* = 13.0 Hz, H-5’), 3.88 (dd, 1H, *J* = 11.7, *J* = 4.3 Hz, H-3), 4.20 (brd, 1H, *J* = 12.7 Hz, H-5’), 4.33 (m, 2H, H-23), 4.39 (dd, 1H, *J* = 10.4, *J* = 3.5 Hz, H-2’), 4.49 (dd, 1H, *J* = 11.9, *J* = 4.8 Hz, H-5”), 4.60 (m, 2H, $CH_2CH=CH_2$), 5.06 (d, 1H, *J* = 6.2 Hz, H-1”), 5.28 (dd, 1H, *J* = 10.5, *J* = 1.0 Hz, $CH_2CH=CH_2$), 5.39 (m, 6H, H-1’, H-2”, H-4”, H-12, $CH_2CH=CH_2$), 5.62 (dd, 1H, *J* = 10.5, *J* = 3.5 Hz, H-3’), 5.69 (m, 1H, H-4’), 5.74 (t, 1H, *J* = 8.4 Hz, H-3”), 5.97 (m, 1H, $CH_2CH=CH_2$). ^{13}C NMR ($CDCl_3$) : δ 13.1 (C-24), 15.8 (C-25), 17.0 (C-26), 21.8 (C-2), 23.6 (C-30), 25.5 (C-27), 33.1 (C-29), 61.0 (C-5’), 62.2 (C-5”), 66.0 (C-23), 69.6 (C-3’), 69.7 (C-4”), 70.2 (C-4’), 70.8 (C-2”), 71.1 (C-3”), 74.8 (C-2’), 78.8 (C-3), 96.7 (C-1’), 102.0 (C-1”), 122.4 (C-12), 143.6 (C-13), 177.3 (C-28). Anal. Calcd for $C_{85}H_{92}O_{18}$: C, 72.84; H, 6.62. Found: C, 72.45; H, 6.43.

4.23. Allyl 3-*O*-[2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzoyl-β-L-arabinopyranosyl]-23-*O*-benzoylhederagenate (39). This compound was prepared at 0 °C using the general method described for **34.** Reaction of allyl hederagenate **33** (0.40 g, 0.65 mmol) and trichloroacetimidate **30** (1.01 g, 0.97 mmol) gave 0.82 g (85%) of **39**. R_f = 0.75 (toluene/acetone 9:1). $[\alpha]_D$ = +83.3° (*c* 1, $CHCl_3$). Selected NMR data: ^{1}H NMR ($CDCl_3$) : δ 0.81 (s, 3H, H-26), 0.94 (s, 3H, H-24), 0.97 (s, 3H, H-29), 1.01 (s, 3H, H-30), 1.04 (s, 3H, H-25), 1.12 (s, 3H, H-27), 2.96 (dd, 1H, *J* = 13.4, *J* = 3.3 Hz, H-18), 3.65 (m, 1H, H-5’’), 3.76 (m, 1H, H-3), 3.77 (t, 1H, *J* = 9.2 Hz, H-3’’), 3.82 (m, 1H, H-5a’), 3.84 (m, 2H, H-6a/b’’), 3.89 (t, 1H, *J* = 9.2 Hz, H-4’’), 4.23 (dl, 1H, *J* = 12.6 Hz, H-5b’), 4.27 (d, 1H, *J* = 11.5 Hz, H-23a), 4.31 (d, 1H, *J* = 11.5 Hz, H-23b), 4.37 (dd, 1H, *J* = 10.5, *J* = 3.6 Hz, H-2’), 4.56 (d, 1H, *J* = 12.0 Hz, CH_2Ph), 4.58 (d, 1H, *J* = 10.9 Hz, CH_2Ph), 4.61 (m, 2H, $CH_2CH=CH_2$), 4.65 (d, 1H, *J* = 11.0 Hz, CH_2Ph), 4.68 (d, 2H, *J* = 11.5 Hz, CH_2Ph), 4.85 (d, 1H, *J* = 7.8 Hz, H-1’’), 4.87 (d, 1H, *J* = 10.8 Hz, CH_2Ph), 5.29 (m, 2H, H-2’’, $CH_2CH=CH_2$), 5.39 (m, 2H, H-1’, $CH_2CH=CH_2$), 5.53 (dd, 1H, *J* = 10.5, *J* = 3.5 Hz, H-3’), 5.67 (m, 1H, H-4’), 5.97 (m, 1H, $CH_2CH=CH_2$). ^{13}C NMR ($CDCl_3$) : δ 13.1 (C-24), 15.7 (C-25), 17.0 (C-26), 22.0 (C-2), 23.6 (C-30), 25.4 (C-27), 33.1 (C-29), 61.0 (C-5’), 66.3 (C-23), 68.8 (C-6’’), 70.0 (C-3’), 70.3 (C-4’), 73.6 (C-2’), 73.7 (C-2’’), 75.1 (C-5’’), 77.8 (C-4’’), 79.6 (C-3), 82.7 (C-3’’), 97.4 (C-1’), 101.6 (C-1’’), 122.5 (C-12), 143.5 (C-13), 177.3 (C-28). Anal. Calcd for $C_{93}H_{104}O_{17}$: C, 74.78; H, 7.02. Found: C, 74.44; H, 7.20.

4.24. Allyl 3-*O*-[2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→2)-2,3-di-*O*-benzoyl-α-L-arabinopyranosyl]-23-*O*-benzoylhederagenate (40). Allyl hederagenate **33** (0.8 g, 1.3 mmol), trichloroacetimidate **27** (2.46 g, 2.6 mmol, 2.0 eq) and 4 Å powdered molecular sieves (7 g) were stirred for 1h at room temperature in dry acetonitrile (20 mL). The mixture was cooled to –35 °C for 30 minutes followed by the rapid addition of a 0.1 M solution of TMSOTf in acetonitrile (3.9 mL, 0.39 mmol, 0.3 eq). The reaction was stirred at this temperature until tlc indicated the disappearance of the allyl hederagenin. Triethylamine was added and the mixture was filtered through Celite and evaporated. The crude residue was purified by column chromatography (toluene/acetone 99:1) to give 0.68 g (38%) of the desired α anomer, and 0.48 g of a mixture of anomeric products. HPLC separation (100% acetonitrile) gave a further 0.36 g (20%) of the desired saponin **40** as a white foam (total yield 58%), and 0.12 g (6%) of the β anomer **38** which was previously described above. R*f* = 0.63 (toluene/acetone 9:1). $[\alpha]_D$ = +47.1° (*c* 1, $CHCl_3$). Selected NMR data: ^{1}H NMR ($CDCl_3$) : δ 0.77 (s, 3H, H-24), 0.79 (s, 3H, H-26), 0.96 (s, 3H, H-29), 0.98 (s, 3H, H-30), 1.02 (s, 3H, H-25), 1.13 (s, 3H, H-27), 2.94 (dd, 1H, *J* = 13.7, *J* = 3.8 Hz, H-18), 3.66 (dd, 1H, *J* = 12.0, *J* = 7.8 Hz, H-5”), 3.73 (dd, 1H, *J* = 11.6, *J* = 4.4 Hz, H-3), 3.84 (dd, 1H, *J* = 11.6, *J* = 3.2 Hz, H-5’), 4.20 (d, 1H, *J* = 11.4 Hz, H-23), 4.27 (dd, 1H, *J* = 11.7, *J* = 7.1 Hz, H-5’), 4.34 (dd, 1H, *J* = 6.0, *J* = 3.9 Hz, H-2’), 4.37 (m, 1H, H-23), 4.41 (dd, 1H, *J* = 12.1, *J* = 4.4 Hz, H-5”), 4.58 (m, 2H, $CH_2CH=CH_2$), 4.89 (d, 1H, *J* = 3.5 Hz, H-1’), 5.14 (d, 1H, *J* = 5.9 Hz, H-1”), 5.26 (d, 1H, *J* = 10.5 Hz, $CH_2CH=CH_2$), 5.32 (m, 1H, H-4”), 5.37 (m, 3H, H-12, H-3’, $CH_2CH=CH_2$), 5.44 (dd, 1H, *J* = 7.7, *J* = 6.1 Hz, H-2”), 5.48 (m, 1H, H-4’), 5.74 (t, 1H, *J* = 7.8 Hz, H-3”), 5.95 (m, 1H, $CH_2CH=CH_2$). ^{13}C NMR ($CDCl_3$) : δ 12.7 (C-24), 15.8 (C-25), 17.0 (C-26), 23.6 (C-30), 25.2 (C-2), 25.4 (C-27), 33.1 (C-29), 59.4 (C-5’), 61.7 (C-5”), 65.7 (C-23), 67.1 (C-4’), 69.2 (C-4”), 70.7

(C-3”, C-2”, C-3’), 75.1 (C-2’), 82.9 (C-3), 101.0 (C-1”), 101.9 (C-1’), 122.3 (C-12), 143.7 (C-13), 177.3 (C-28). Anal. Calcd for $C_{85}H_{92}O_{18}$: C, 72.84; H, 6.62. Found: C, 72.69; H, 6.84.

4.25. Allyl 3-*O*-[2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-arabinopyranosyl]-23-*O*-benzoylhederagenate (41). This product was prepared in acetonitrile as described for compound **40.** Reaction of allyl hederagenate **33** (0.83 g, 1.3 mmol) and trichloroacetimidate **30** (2.8 g, 2.7 mmol) gave 1.22 g (61%) of **41** as well as 0.28 g (14%) of the β coupling product **39**. R_f = 0.69 (toluene/acetone 9:1). $[\alpha]_D$ = +47.5° (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) : δ 0.73 (s, 3H, H-24), 0.76 (s, 3H, H-26), 0.95 (s, 3H, H-29), 0.97 (s, 3H, H-25), 0.98 (s, 3H, H-30), 1.07 (s, 3H, H-27), 2.92 (dd, 1H, *J* = 13.7, *J* = 3.8 Hz, H-18), 3.64 (dt, *J* = 9.7, *J* = 3.3 Hz, H-5’’), 3.69 (dd, 1H, *J* = 11.7, *J* = 4.6 Hz, H-3), 3.75 (t, 1H, *J* = 9.2 Hz, H-3’’), 3.78 (m, 1H, H-5a’), 3.80 (m, 2H, H-6a/b’’), 3.85 (t, 1H, *J* = 9.2 Hz, H-4’’), 4.20 (dd, 1H, *J* = 12.0, *J* = 6.4 Hz, H-5b’), 4.27 (d, 1H, *J* = 11.4 Hz, H-23a), 4.32 (m, 2H, H-2’, H-23b), 4.57 (m, 4H, $CH_2CH{=}CH_2$, CH_2Ph), 4.60 (m, 2H, CH_2Ph), 4.69 (d, 1H, *J* = 11.2 Hz, CH_2Ph), 4.82 (m, 1H, H-1’), 4.83 (d, 1H, *J* = 10.8 Hz, CH_2Ph), 4.89 (d, 1H, *J* = 8.0 Hz, H-1’’), 5.25 (m, 2H, H-3’, $CH_2CH{=}CH_2$), 5.31 (dd, 1H, *J* = 9.4, *J* = 8.1 Hz, H-2’’), 4.35 (m, 1H, H-12), 4.36 (m, 1H, $CH_2CH{=}CH_2$), 4.38 (m, 1H, H-4’), 5.95 (m, 1H, $CH_2CH{=}CH_2$). ^{13}C NMR ($CDCl_3$) : δ 12.8 (C-24), 15.6 (C-25), 17.0 (C-26), 23.6 (C-30), 25.1 (C-2), 25.4 (C-27), 33.1 (C-29), 60.2 (C-5’), 65.9 (C-23), 67.4 (C-4’), 69.1 (C-6’’), 71.8 (C-3’), 73.4 (C-2’’), 74.7 (C-2’), 75.5 (C-5’’), 77.8 (C-4’’), 82.7 (C-3’’), 82.8 (C-3), 101.4 (C-1’’), 101.9 (C-1’), 122.3 (C-12), 143.7 (C-13), 177.3 (C-28). Anal. Calcd for $C_{93}H_{104}O_{17}$: C, 74.78; H, 7.02. Found: C, 74.44; H, 7.31.

4.26. 3-*O*-[β-D-xylopyranosyl-(1→2)-α-L-arabinopyranosyl]hederagenin (1). General method 1. In a typical experiment, $Pd(PPh_3)_4$ (0.57 g, 0.49 mmol, 1.0 eq) was added to a solution of saponin **40** (0.680 g, 0.49 mmol) in 3% KOH in MeOH (39 mL). After heating to 60 °C for 6h, the reaction was neutralized with Amberlite IR 120 (H^+ form), filtered and evaporated. The crude residue was purified by column chromatography (CH_2Cl_2/MeOH 9:1 to 8:2) to give 0.280 g (76%) of the deprotected saponin **1** as an amorphous solid.

General method 2. Use of a catalytic amount of $Pd(PPh_3)_4$: in a typical experiment $Pd(PPh_3)_4$ (0.025 g, 0.02 mmol, 0.3 eq) was added to a solution of saponin **40** (0.102 g, 0.07 mmol) in a THF/3% KOH in MeOH (1:1) mixture (6 mL). After heating to 60 °C for 7h, the reaction was neutralized with Amberlite IR 120 (H^+ form), filtered and evaporated. The crude residue was purified by column chromatography (CH_2Cl_2/MeOH 9:1 to 8:2) to give 0.048 g (89%) of the deprotected saponin **1** as an amorphous solid.

$[\alpha]_D$ = +41.0° (*c* 0.5, pyridine). ^{1}H NMR (pyridine-d_5) : δ 0.90 (s, 3H, H-29), 0.93 (s, 3H, H-25), 0.98 (s, 3H, H-30), 1.00 (s, 6H, H-24, H-26), 1.03-2.22 (m, 22H, H-1, H-2, H-5, H-6, H-7, H-9, H-11, H-15, H-16, H-19, H-21, H-22), 1.22 (s, 3H, H-27), 3.26 (dd, 1H, *J* = 13.6, *J* = 3.8 Hz, H-18), 3.56 (m, 1H, H-5''), 3.64 (brd, 1H, *J* = 11.1 Hz, H-5'), 3.68 (d, 1H, *J* = 11.0 Hz, H-23), 4.08 (m, 1H, H-2''), 4.10 (m, 1H, H-3''), 4.15 (dd, 1H, *J* = 8.4, *J* = 2.3 Hz, H-3'), 4.18 (m, 1H, H-4''), 4.24 (m, 1H, H-5'), 4.25 (m, 1H, H-4'), 4.27 (m, 1H, H-3), 4.31 (dd, 1H, *J* = 11.4, *J* = 5.2 Hz, H-5''), 4.35 (d, 1H, *J* = 11.1 Hz, H-23), 4.53 (brt, 1H, *J* = 7.5 Hz, H-2'), 5.07 (d, 1H, *J* = 6.5 Hz, H-1''), 5.11 (d, 1H, *J* = 6.6 Hz, H-1'), 5.46 (m, 1H, H-12). ^{13}C NMR (pyridine-d_5) : δ 12.9 (C-24), 15.8 (C-25), 17.1 (C-26), 17.8 (C-6), 23.3 (C-16), 23.4 (C-30), 23.5 (C-11), 25.9 (C-27), 26.0 (C-2), 28.0 (C-15), 30.6 (C-20), 32.5 (C-7), 32.9 (C-22, C-29), 33.8 (C-21), 36.6 (C-10), 38.5 (C-1), 39.4 (C-8), 41.6 (C-18), 41.8 (C-14), 43.3 (C-4), 46.1 (C-19), 46.3 (C-17), 47.0 (C-5), 47.8 (C-9), 63.2 (C-23), 65.6 (C-5'), 67.1 (C-5''), 68.4 (C-4'), 70.6 (C-4''), 73.6 (C-3'), 75.8 (C-2''), 77.9 (C-3''), 81.1 (C-3), 81.5 (C-2'), 104.2 (C-1'), 106.4 (C-1''), 122.3 (C-12), 144.5 (C-13), 179.9 (C-28). HRMS: $C_{40}H_{64}O_{12}Na$ calcd 759.4295; found 759.4316.

4.27. 3-*O*-[β-D-xylopyranosyl-(1→2)-β-L-arabinopyranosyl]hederagenin (2). Using a stoichiometric amount of $Pd(PPh_3)_4$ in the general deprotection method 1 described for **1**, the deprotection of saponin **38** (0.52 g, 0.37 mmol) gave 0.17 g (64%) of **2**. Use of the catalytic method with 0.115 g (0.08 mmol) of **38** gave 0.050 g (84%) of **2**. $[\alpha]_D$ = +82.2° (*c* 0.5, pyridine). Selected NMR data: ^{1}H NMR (pyridine- d_5) : δ 0.85 (s, 3H, H-24), 0.85 (s, 3H, H-25), 0.92 (s, 3H, H-29), 0.99 (s, 3H, H-30), 1.00 (s, 3H, H-26), 1.24 (s, 3H, H-27), 3.27 (dd, 1H, *J* = 13.5, *J* = 3.6 Hz, H-18), 3.50 (dd, 1H, *J* = 11.0, *J* = 10.1 Hz, H-5''), 3.70 (d, 1H, *J* = 10.7 Hz, H-23), 3.93 (d, 1H, *J* = 10.9 Hz, H-23), 4.10 (dd, 1H, *J* = 8.7, *J* = 7.0 Hz, H-2''), 4.12 (dd, 1H, *J* = 10.5, *J* = 1.7 Hz, H-5'; t, 1H, *J* = 8.6 Hz, H-3''), 4.18 (m, 1H, H-4''), 4.21 (dd, 1H, *J* = 11.9, *J* = 4.8 Hz, H-3), 4.25 (dd, 1H, *J* = 11.3, *J* = 5.1 Hz, H-5''), 4.43 (m, 1H, H-4'), 4.44 (brd, 1H, *J* = 11.3 Hz, H-5'), 4.62 (dd, 1H, *J* = 9.9, *J* = 3.1 Hz, H-3'), 4.67 (dd, 1H, *J* = 9.9, *J* = 3.2 Hz, H-2'), 5.00 (d, 1H, *J* = 7.1 Hz, H-1''), 5.48 (m, 1H, H-12), 5.69 (d, 1H, *J* = 3.3 Hz, H-1'). ^{13}C NMR (pyridine-d_5) : δ 13.8 (C-24), 15.6 (C-25), 17.2 (C-26), 22.2 (C-2), 23.5 (C-30), 25.9 (C-27), 33.0 (C-29), 64.0 (C-23), 64.3 (C-5'), 66.6 (C-5''), 69.2 (C-3'), 70.0 (C-4'), 70.5 (C-4''), 74.8 (C-2''), 77.4 (C-3), 77.5 (C-3''), 79.4 (C-2'), 97.6 (C-1'), 106.6 (C-1''), 122.3 (C-12), 144.6 (C-13), 180.3 (C-28). HRMS: $C_{40}H_{64}O_{12}Na$ calcd 759.4295; found 759.4275.

4.28. 3-*O*-[β-D-xylopyranosyl-(1→3)-α-L-arabinopyranosyl]hederagenin (3). Using a stoichiometric amount of $Pd(PPh_3)_4$ in the general deprotection method 1 described for **1**, the deprotection of saponin **34** (0.26 g, 0.18 mmol) gave 0.11 g (82%) of **3**. Use of the catalytic method with 0.055 g (0.04 mmol) of **34** gave 0.021 g (72%) of **3**. $[\alpha]_D = +47.6°$ (*c* 0.5, pyridine). Selected NMR data: ^{1}H NMR (pyridine-d_5) : δ 0.91 (s, 3H, H-25), 0.92 (s, 3H, H-24), 0.92 (s, 3H, H-29), 0.98 (s, 3H, H-30), 1.00 (s, 3H, H-26), 1.24 (s, 3H, H-27), 3.27 (dd, 1H, *J* = 13.7, *J* = 3.7 Hz, H-18), 3.70 (d, 1H, *J* = 10.7 Hz, H-23), 3.71 (m, 1H, H-5''), 3.75 (brd, 1H, *J* = 11.6 Hz, H-5'), 4.03 (dd, 1H, *J* = 8.8, *J* = 7.7 Hz, H-2''), 4.10 (dd, 1H, *J* = 9.4, *J* = 3.3 Hz, H-3'), 4.18 (m, 2H, H-3'', H-4''), 4.26 (dd, 1H, *J* = 12.0, *J* = 2.0 Hz, H-5'), 4.29 (dd, 1H, *J* = 12.2, *J* = 4.6 Hz, H-3), 4.32 (d, 1H, *J* = 10.6 Hz, H-23), 4.33 (dd, 1H, *J* = 10.7, *J* = 5.2 Hz, H-5''), 4.39 (m, 1H, H-4'), 4.59 (dd, 1H, *J* = 9.2, *J* = 7.7 Hz, H-2'), 5.04 (d, 1H, *J* = 7.5 Hz, H-1'), 5.20 (d, 1H, *J* = 7.6 Hz, H-1''), 5.47 (m, 1H, H-12). ^{13}C NMR (pyridine-d_5) : δ 13.4 (C-24), 15.8 (C-25), 17.2 (C-26), 23.5 (C-30), 25.9 (C-27), 33.0 (C-29), 63.6 (C-23), 66.7 (C-5'), 66.8 (C-5''), 69.0 (C-4'), 70.6 (C-4''), 71.5 (C-2'), 74.9 (C-2''), 77.5 (C-3''), 81.5 (C-3), 83.3 (C-3'), 106.2 (C-1'), 106.3 (C-1''), 122.3 (C-12), 144.5 (C-13), 180.2 (C-28). HRMS: $C_{40}H_{64}O_{12}Na$ calcd 759.4295; found 759.4303.

4.29. 3-*O*-[β-D-xylopyranosyl-(1→4)-α-L-arabinopyranosyl]hederagenin (4). Using a stoichiometric amount of $Pd(PPh_3)_4$ in the general deprotection method 1 described for **1**, the deprotection of saponin **35** (0.32 g, 0.23 mmol) gave 0.14 g (84%) of **4**. Use of the catalytic method with 0.108 g (0.08 mmol) of **35** gave 0.042 g (74%) of **4**. $[\alpha]_D = +46.8°$ (*c* 0.5, pyridine). Selected NMR data: ^{1}H NMR (pyridine- d_5) : δ 0.88 (s, 3H, H-24), 0.92 (s, 6H, H-25, H-29), 0.98 (s, 3H, H-30), 0.99 (s, 3H, H-26), 1.23 (s, 3H, H-27), 3.27 (dd, 1H, *J* = 13.7, *J* = 3.8 Hz, H-18), 3.64 (brt, 1H, *J* = 10.6 Hz, H-5''), 3.67 (d, 1H, *J* = 10.7 Hz, H-23), 3.76 (brd, 1H, *J* = 11.6 Hz, H-5'), 4.02 (dd, 1H, *J* = 8.7, *J* = 7.9 Hz, H-2''), 4.13 (t, 1H, *J* = 8.8 Hz, H-3''), 4.15 (dd, 1H, *J* = 9.3, *J* = 3.6 Hz, H-3'), 4.20 (m, 1H, H-4''), 4.23 (dd, 1H, *J* = 12.2, *J* = 4.6 Hz, H-3), 4.26 (brd, 1H, *J* = 11.1 Hz, H-23), 4.27 (m, 1H, H-4'), 4.30 (dd, 1H, *J* = 11.3, *J* = 5.2 Hz, H-5''), 4.40 (dd, 1H, *J* = 9.1, *J* = 7.4 Hz, H-2'), 4.43 (dd, 1H, *J* = 12.5, *J* = 2.2 Hz, H-5'), 4.96 (d, 1H, *J* = 7.3 Hz, H-1'), 5.06 (d, 1H, *J* = 7.7 Hz, H-1''), 5.47 (m, 1H, H-12). ^{13}C NMR (pyridine-d_5) : δ 13.3 (C-24), 15.8 (C-25), 17.2 (C-26), 23.5 (C-30), 25.9 (C-27), 33.0 (C-29), 63.9 (C-23), 66.0 (C-5'), 66.9 (C-5''), 70.5 (C-4''), 73.1 (C-2'), 74.0 (C-3'), 75.0 (C-2''), 77.8 (C-3''), 79.2 (C-4'), 81.8 (C-3), 106.1 (C-1'), 106.8 (C-1''), 122.3 (C-12), 144.5 (C-13), 180.1 (C-28). HRMS: $C_{40}H_{64}O_{12}Na$ calcd 759.4295; found 759.4266.

4.30. 3-*O*-[β-D-glucopyranosyl-(1→2)-α-L-arabinopyranosyl]hederagenin (5). General method 1. In a typical experiment, $Pd(PPh_3)_4$ (0.57 g, 0.49 mmol, 1.0 eq) was added to a solution of saponin **41** (0.730 g, 0.49 mmol) in 3% KOH in MeOH (39 mL). After heating to 60 °C for 6h, the reaction was neutralized with Amberlite IR 120 (H^+ form), filtered and evaporated. The crude residue was taken up in ethanol (84 mL) and Pd/C (2.51 g) was added. The reaction then was placed under H_2. After stirring for 48h at room temperature, the mixture was filtered over celite, evaporated, and the crude saponin purified by column chromatography (CH_2Cl_2/MeOH 9:1 to 8:2) to give 0.37 g (82%) of the desired product **5** as an amorphous solid.

General method 2. Use of a catalytic amount of $Pd(PPh_3)_4$: in a typical experiment $Pd(PPh_3)_4$ (0.031 g, 0.03 mmol, 0.3 eq) was added to a solution of saponin **41** (0.132 g, 0.09 mmol) in a THF/3% KOH in MeOH (1:1) mixture (6 mL). After heating to 60 °C for 7h, the reaction was neutralized with Amberlite IR 120 (H^+ form), filtered and evaporated. The crude residue was rapidly passed through a silica gel column to remove non-polar impurities (CH_2Cl_2/MeOH, 9.8:0.2) and the partially protected saponin was taken up in ethanol (7 mL) and Pd/C (0.080 g) was added. The reaction then was placed under H_2. After stirring for 24-48hrs at room temperature, the mixture was filtered over celite, evaporated, and the crude saponin purified by column chromatography ($CHCl_3$/MeOH 9:1 to 8:2) to give 0.059 g (87%) of the desired product **5** as an amorphous solid. ^{1}H NMR (pyridine-d_5) : δ 0.89 (s, 3H, H-25), 0.91 (s, 3H, H-29), 0.97 (s, 6H, H-30, H-26), 0.98-2.15 (m, 22H, H-1, H-2, H-5, H-6, H-7, H-9, H-11, H-15, H-16, H-19, H-21, H-22), 1.00 (s, 3H, H-24), 1.20 (s, 3H, H-27), 3.27 (dd, 1H, *J* = 13.6, *J* = 3.7 Hz, H-18), 3.70 (brd, 1H, *J* = 10.7 Hz, H-5a’), 3.73 (d, 1H, *J* = 10.8 Hz, H-23a), 3.81 (m, 1H, H-5’’), 4.09 (t, 1H, *J* = 8.0 Hz, H-2’’), 4.16 (dd, 1H, *J* = 7.5, *J* = 4.5 Hz, H-3), 4.18 (t, 1H, *J* = 8.1 Hz, H-3’’), 4.22 (m, 2H, H-23b, H-4’’), 4.27 (dd, 1H, *J* = 7.0, *J* = 3.7 Hz, H-3’), 4.28 (m, 1H, H-5b’), 4.32 (m, 1H, H-4’), 4.35 (dd, 1H, *J* = 11.7, *J* = 4.5 Hz, H-6a’’), 4.47 (dd, 1H, *J* = 11.7, *J* = 1.6 Hz, H-6b’’), 4.60 (t, 1H, *J* = 6.7 Hz, H-2’), 5.19 (d, 1H, *J* = 4.6 Hz, H-1’), 5.20 (d, 1H, *J* = 7.0 Hz, H-1’’), 5.45 (m, 1H, H-12). ^{13}C NMR (pyridine-d_5) : δ 13.2 (C-24), 15.7 (C-25), 17.2 (C-26), 17.8 (C-6), 23.4 (C-16), 23.5 (C-30), 23.5 (C-11), 25.7 (C-2), 25.8 (C-27), 28.0 (C-15), 30.6 (C-20), 32.5 (C-7), 32.9 (C-22), 33.0 (C-29), 34.9 (C-21), 36.6 (C-10), 38.3 (C-1), 39.4 (C-8), 41.6 (C-18), 41.8 (C-14), 43.2 (C-4), 46.3 (C-19), 46.3 (C-17), 47.4 (C-5), 47.8 (C-9), 62.1 (C-6’’), 64.3 (C-23), 64.8 (C-5’), 67.9 (C-4’), 71.0 (C-4’’), 73.2 (C-3’), 75.8 (C-2’’), 77.7 (C-3’’), 78.0 (C-5’’), 80.7 (C-2’), 81.8 (C-3), 103.7 (C-1’), 105.4 (C-1’’), 122.2 (C-12), 144.6 (C-13). HRMS: $C_{41}H_{66}O_{13}Na$ calcd 789.4401; found 789.4415.

4.31. 3-*O*-[β-D-glucopyranosyl-(1→2)-β-L-arabinopyranosyl]hederagenin (6). Using a stoichiometric amount of $Pd(PPh_3)_4$ in the general deprotection method 1 described for **5**, the deprotection of saponin **39** (0.89 g, 0.60 mmol) gave 0.40 g (88%) of **6**. Use of the catalytic method with 0.145 g (0.10 mmol) of **39** gave 0.061 g (82%) of **6**. $[\alpha]_D$ = +74.6° (*c* 0.5, pyridine). Selected NMR data: ^{1}H NMR (pyridine-d_5) : δ 0.83 (s, 3H, H-25), 0.85 (s, 3H, H-24), 0.92 (s, 3H, H-29), 0.98 (s, 6H, H-26, H-30), 1.20 (s, 3H, H-27), 3.27 (dd, 1H, *J* = 13.7, *J* = 3.6 Hz, H-18), 3.68 (d, 1H, *J* = 10.6 Hz, H-23a), 3.77 (ddd, 1H, *J* = 8.8, *J* = 5.4, *J* = 2.6 Hz, H-5’’), 3.94 (d, 1H, *J* = 10.8 Hz, H-23b), 4.06 (dd, 1H, *J* = 12.0, *J* = 1.8 Hz, H-5a’), 4.12 (dd, 1H, *J* = 9.2, *J* = 7.8 Hz, H-2’’), 4.15 (m, 1H, H-4’’), 4.16 (m, 1H, H-3’’), 4.23 (dd, 1H, *J* = 11.8, *J* = 4.4 Hz, H-3), 4.30 (dd, 1H, *J* = 11.7, *J* =

5.4 Hz, H-6a’’), 4.39 (m, 1H, H-4’), 4.44 (m, 2H, H-6b’’, H-5b’), 4.65 (dd, 1H, *J* = 9.9, *J* = 3.3 Hz, H-3’), 4.73 (dd, 1H, *J* = 9.9, *J* = 3.2 Hz, H-2’), 5.12 (d, 1H, *J* = 7.5 Hz, H-1’’), 5.45 (m, 1H, H-12), 5.82 (d, 1H, *J* = 3.3 Hz, H-1’). ^{13}C NMR (pyridine-d_5) : δ 13.8 (C-24), 15.6 (C-25), 17.2 (C-26), 22.2 (C-2), 23.5 (C-30), 25.8 (C-27), 33.0 (C-29), 62.4 (C-6’’), 64.2 (C-23), 64.3 (C-5’), 69.2 (C-3’), 70.0 (C-4’), 71.3 (C-4’’), 75.2 (C-2’’), 77.3 (C-3), 77.9 (C-3’’), 77.9 (C-5’’), 79.9 (C-2’), 97.7 (C-1’), 106.0 (C-1’’), 122.2 (C-12), 144.6 (C-13). HRMS: $C_{41}H_{66}O_{13}Na$ calcd 789.4401; found 789.4374.

4.32. 3-*O*-[β-D-glucopyranosyl-(1→3)-α-L-arabinopyranosyl]hederagenin (7). Using a stoichiometric amount of $Pd(PPh_3)_4$ in the general deprotection method 1 described for **5**, the deprotection of saponin **36** (0.67 g, 0.43 mmol) gave 0.27 g (78%) of **7**. Use of the catalytic method with 0.060 g (0.04 mmol) of **36** gave 0.026 g (84%) of **7**. $[\alpha]_D$ = +46.8° (*c* 0.5, pyridine). Selected NMR data: ^{1}H NMR (pyridine-d_5) : δ 0.90 (s, 6H, H-25, H-24), 0.91 (s, 3H, H-29), 0.98 (s, 3H, H-30), 0.99 (s, 3H, H-26), 1.24 (s, 3H, H-27), 3.27 (dd, 1H, *J* = 13.8, *J* = 4.2, H-18), 3.67 (brd, 1H, *J* = 12.0, H-5a’), 3.70 (d, 1H, *J* = 11.0, H-23a), 4.00 (ddd, 1H, *J* = 9.5, *J* = 5.3, *J* = 1.9, H-5’’), 4.07 (t, 1H, *J* = 8.4, H-2’’), 4.15 (m, 1H, H-3’), 4.18 (t, 1H, *J* = 9.1, H-4’’; m, 1H, H-5b’), 4.26 (m, 1H, H-3), 4.27 (t, 1H, *J* = 8.9, H-3’’), 4.32 (d, 1H, *J* = 11.4, H-23b), 4.33 (brd, 1H, *J* = 11.8, H-6a’’), 4.44 (m, 1H, H-4’), 4.54 (dd, 1H, *J* = 11.8, *J* = 1.8, H-6b’’), 4.58 (dd, 1H, *J* = 9.0, *J* = 7.8, H-2’), 5.01 (d, 1H, *J* = 7.5, H-1’), 5.29 (d, 1H, *J* = 7.8, H-1’’), 5.47 (m, 1H, H-12). ^{13}C NMR (pyridine-d_5) : δ 14.5 (C-24), 16.8 (C-25), 18.3 (C-26), 24.6 (C-30), 26.9 (C-27), 27.0 (C-2), 34.0 (C-29), 63.2 (C-6’’), 64.8 (C-23), 67.7 (C-5’), 69.9 (C-4’), 72.2 (C-4’’), 72.6 (C-2’), 76.2 (C-2’’), 78.8 (C-3’’), 79.3 (C-5’’), 82.6 (C-3), 84.8 (C-3’), 106.7 (C-1’’), 107.2 (C-1’’), 123.3 (C-12), 145.6 (C-13). HRMS: $C_{41}H_{66}O_{13}Na$ calcd 789.4401; found 789.4391.

3-*O*-[β-D-glucopyranosyl-(1→4)-α-L-arabinopyranosyl]hederagenin (8). Using a stoichiometric amount of $Pd(PPh_3)_4$ in the general deprotection method 1 described for **5**, the deprotection of saponin **37** (0.80 g, 0.50 mmol) gave 0.34 g (82%) of **8**. Use of the catalytic method with 0.122 g (0.08 mmol) of **37** gave 0.041 g (65%) of **8**. $[\alpha]_D$ = +35.5° (*c* 0.53, CH_3OH). Selected NMR data: ^{1}H NMR (pyridine-d_5) : δ 0.89 (s, 3H, H-24), 0.91 (s, 3H, H-29), 0.91 (s, 3H, H-25), 0.98 (s, 3H, H-30), 0.99 (s, 3H, H-26), 1.23 (s, 3H, H-27), 3.27 (dd, 1H, *J* = 13.6, *J* = 3.6 Hz, H-18), 3.67 (d, 1H, *J* = 10.6 Hz, H-23a), 3.68 (brd, 1H, *J* = 11.8 Hz, H-5a’), 3.94 (m, 1H, H-5’’), 4.05 (m, 1H, H-2’’), 4.10 (dd, 1H, *J* = 9.2, *J* = 3.4 Hz, H-3’), 4.21 (m, 1H, H-3), 4.22 (m, 2H, H-3’’, H-4’’), 4.27 (d, 1H, *J* = 11.0 Hz, H-23b), 4.32 (m, 1H, H-4’), 4.35 (dd, 1H, *J* = 12.0, *J* = 5.3 Hz, H-6a’’), 4.41 (dd, 1H, *J* = 8.9, *J* = 7.6 Hz, H-2’), 4.44 (m, 1H, H-5b’), 4.51 (dd, 1H, *J* = 11.9, *J* = 1.8 Hz, H-6b’’), 4.94 (d, 1H, *J* = 7.3 Hz, H-1’), 5.23 (d, 1H, *J* = 7.8 Hz, H-1’’), 5.44 (m, 1H, H-12). ^{13}C NMR (pyridine-d_5) :

δ 13.3 (C-24), 15.8 (C-25), 17.2 (C-26), 23.5 (C-30), 25.8 (C-2), 25.9 (C-27), 33.0 (C-29), 62.1 (C-6''), 63.9 (C-23), 66.0 (C-5'), 70.9 (C-4''), 73.2 (C-2'), 74.2 (C-3'), 75.3 (C-2''), 77.9 (C-3''), 78.3 (C-5''), 79.4 (C-4'), 81.8 (C-3), 106.1 (C-1'), 106.4 (C-1''), 122.2 (C-12), 144.6 (C-13). HRMS: $C_{41}H_{66}O_{13}Na$ calcd 789.4401; found 789.4409.

The saponins **1-8** were treated with excess diazomethane[26] to give their corresponding methyl esters in quantitative yields.

4.34. Methyl 3-*O*-[β-D-xylopyranosyl-(1→2)-α-L-arabinopyranosyl]hederagenate (1a). $[\alpha]_D$ = +39.0° (*c* 0.5, pyridine). ^{1}H NMR (CD_3OD) : δ 0.72 (s, 3H, H-24), 0.77 (s, 3H, H-26), 0.93 (s, 3H, H-29), 0.96 (s, 3H, H-30), 0.97-2.06 (m, 22H, H-1, H-2, H-5, H-6, H-7, H-9, H-11, H-15, H-16, H-19, H-21, H-22), 1.00 (s, 3H, H-25), 1.19 (s, 3H, H-27), 2.89 (dd, 1H, *J* = 13.7, *J* = 3.9 Hz, H-18), 3.18 (dd, 1H, *J* = 11.1, *J* = 10.7 Hz, H-5''), 3.23 (dd, 1H, *J* = 9.1, *J* = 7.7 Hz, H-2''), 3.26 (d, 1H, *J* = 10.1 Hz, H-23), 3.33 (m, 1H, H-3''), 3.48 (ddd, 1H, *J* = 10.2, *J* = 8.9, *J* = 5.4 Hz, H-4''), 3.54 (dd, 1H, *J* = 13.2, *J* = 2.6 Hz, H-5'), 3.61 (dd, 1H, *J* = 12.3, *J* = 4.8 Hz, H-3), 3.64 (s, 3H, OCH_3), 3.72 (m, 1H, H-23), 3.74 (m, 1H, H-3'), 3.75 (m, 1H, H-2'), 3.84 (m, 3H, H-5'', H-4', H-5'), 4.48 (d, 1H, *J* = 6.4 Hz, H-1'), 4.51 (d, 1H, *J* = 7.6 Hz, H-1''), 5.27 (m, 1H, H-12). ^{13}C NMR (CD_3OD) : δ 11.6 (C-24), 14.9 (C-25), 16.2 (C-26), 17.3 (C-6), 22.5 (C-30), 22.6 (C-16), 23.1 (C-11), 25.0 (C-27), 25.0 (C-2), 27.3 (C-15), 30.1 (C-20), 31.8 (C-7), 32.1 (C-29), 32.1 (C-22), 33.3 (C-21), 36.2 (C-10), 38.0 (C-1), 39.1 (C-8), 41.3 (C-18), 41.4 (C-14), 42.6 (C-4), 45.6 (C-19), 46.4 (C-5), 46.6 (C-17), 47.5 (C-9), 50.7 (OCH_3), 62.8 (C-23), 64.7 (C-5'), 65.7 (C-5''), 68.0 (C-4'), 69.7 (C-4''), 72.6 (C-3'), 74.5 (C-2''), 76.4 (C-3''), 79.6 (C-2'), 81.5 (C-3), 103.3 (C-1'), 104.8 (C-1''), 122.3 (C-12), 143.6 (C-13), 178.6 (C-28). HRMS: $C_{41}H_{66}O_{12}Na$ calcd 773.4452; found 773.4425.

4.35. Methyl 3-*O*-[β-D-xylopyranosyl-(1→2)-β-L-arabinopyranosyl]hederagenate (2a). $[\alpha]_D$ = +87.2° (*c* 0.5, pyridine). Selected NMR data: ^{1}H NMR (CD_3OD) : δ 0.69 (s, 3H, H-24), 0.77 (s, 3H, H-26), 0.93 (s, 3H, H-30), 0.96 (s, 3H, H-29), 1.00 (s, 3H, H-25), 1.19 (s, 3H, H-27), 2.89 (dd, 1H, *J* = 13.7, *J* = 4.1 Hz, H-18), 3.21 (dd, 1H, *J* = 11.3, *J* = 10.4 Hz, H-5''), 3.27 (dd, 1H, *J* = 9.0, *J* = 7.4 Hz, H-2''), 3.33 (m, 1H, H-23), 3.34 (t, 1H, *J* = 8,9 Hz, H-3''), 3.47 (d, 1H, *J* = 11.2 Hz, H-23), 3.50 (m, 1H, H-4''), 3.59 (dd, 1H, *J* = 12.4, *J* = 1.2 Hz, H-5'), 3.64 (s, 3H, OCH_3), 3.65 (dd, 1H, *J* = 11.4, *J* = 4.7 Hz, H-3), 3.83 (dd, 1H, *J* = 9.3, *J* = 3.4 Hz, H-2'), 3.88 (dd, 1H, *J* = 11.4, *J* = 5.3 Hz, H-5''), 3.94 (m, 1H, H-4'), 3.95 (m, 1H, H-3'), 3.98 (brd, 1H, *J* = 12.2 Hz, H-5'), 4.41 (d, 1H, *J* = 7.4 Hz, H-1''), 5.14 (d, 1H, *J* = 3.4 Hz, H-1'), 5.28 (m, 1H, H-12). ^{13}C NMR (CD_3OD) : δ 12.4 (C-24), 14.8 (C-25), 16.2 (C-26), 21.6 (C-2), 22.5 (C-30), 25.0 (C-27), 32.1 (C-29), 50.7 (OCH_3), 63.2 (C-5'), 63.5 (C-23), 65.4 (C-5''), 68.1 (C-3'), 69.4 (C-4'), 69.7 (C-4''), 73.9 (C-2''), 76.3 (C-3''), 77.2

(C-3), 78.4 (C-2’), 97.0 (C-1’), 105.4 (C-1”), 122.3 (C-12), 143.6 (C-13), 178.6 (C-28). HRMS: $C_{41}H_{66}O_{12}Na$ calcd 773.4452; found 773.4456.

4.36. Methyl 3-*O*-[β-D-xylopyranosyl-(1→3)-α-L-arabinopyranosyl]hederagenate (3a). $[\alpha]_D$ = +49.0° (*c* 0.5, pyridine). Selected NMR data: ^{1}H NMR (CD_3OD) : δ 0.74 (s, 3H, H-24), 0.77 (s, 3H, H-26), 0.93 (s, 3H, H-29), 0.96 (s, 3H, H-30), 1.00 (s, 3H, H-25), 1.19 (s, 3H, H-27), 2.89 (dd, 1H, *J* = 13.5, *J* = 3.4 Hz, H-18), 3.23 (dd, 1H, *J* = 11.0, *J* = 10.7 Hz, H-5”), 3.31 (m, 1H, H-23), 3.32 (m, 1H, H-2”), 3.36 (t, 1H, *J* = 8.2 Hz, H-3”), 3.52 (m, 1H, H-4”), 3.58 (brd, 1H, *J* = 12.4 Hz, H-5’), 3.63 (m, 2H, H-3, H-3’), 3.64 (s, 3H, OC*H*$_3$), 3.65 (m, 1H, H-23), 3.71 (dd, 1H, *J* = 9.3, *J* = 7.6 Hz, H-2’), 3.87 (dd, 1H, *J* = 12.4, *J* = 2.0 Hz, H-5’), 3.88 (dd, 1H, *J* = 11.3, *J* = 5.4 Hz, H-5”), 3.97 (m, 1H, H-4’), 4.36 (d, 1H, *J* = 7.5 Hz, H-1’), 4.53 (d, 1H, *J* = 7.1 Hz, H-1”), 5.27 (m, 1H, H-12). ^{13}C NMR (CD_3OD) : δ 11.9 (C-24), 15.0 (C-25), 16.2 (C-26), 22.5 (C-30), 25.1 (C-27), 32.1 (C-29), 50.8 (O*C*H$_3$), 63.6 (C-23), 65.4 (C-5’), 65.5 (C-5”), 68.3 (C-4’), 69.6 (C-4”), 70.7 (C-2’), 73.7 (C-2”), 76.0 (C-3”), 82.0 (C-3), 82.2 (C-3’), 104.7 (C-1’, C-1”), 122.3 (C-12), 143.6 (C-13), 178.5 (C-28). HRMS: $C_{41}H_{66}O_{12}Na$ calcd 773.4452; found 773.4450.

4.37. Methyl 3-*O*-[β-D-xylopyranosyl-(1→4)-α-L-arabinopyranosyl]hederagenate (4a). $[\alpha]_D$ = +45.2° (*c* 0.5, pyridine). Selected NMR data: ^{1}H NMR (CD_3OD) : δ 0.69 (s, 3H, H-24), 0.73 (s, 3H, H-26), 0.89 (s, 3H, H-29), 0.92 (s, 3H, H-30), 0.96 (s, 3H, H-25), 1.15 (s, 3H, H-27), 2.85 (dd, 1H, *J* = 13.7, *J* = 3.8 Hz, H-18), 3.16 (dd, 1H, *J* = 11.0, *J* = 10.8 Hz, H-5”), 3.25 (m, 1H, H-2”), 3.26 (d, 1H, *J* = 11.4 Hz, H-23), 3.29 (m, 1H, H-3”), 3.46 (m, 1H, H-4”), 3.50 (m, 1H, H-2’), 3.51 (m, 1H, H-5’), 3.53 (m, 1H, H-3’), 3.58 (dd, 1H, *J* = 11.5, *J* = 4.7 Hz, H-3), 3.59 (m, 1H, H-23), 3.60 (s, 3H, OC*H*$_3$), 3.85 (dd, 1H, *J* = 11.4, *J* = 5.3 Hz, H-5”), 3.83 (m, 1H, H-4’), 4.03 (dd, 1H, *J* = 12.6, *J* = 2.4 Hz, H-5’), 4.28 (d, 1H, *J*= 6.4 Hz, H-1’), 4.39 (d, 1H, *J* = 7.1 Hz, H-1”), 5.23 (m, 1H, H-12). ^{13}C NMR (CD_3OD) : δ 11.9 (C-24), 14.9 (C-25), 16.2 (C-26), 22.5 (C-30), 25.0 (C-27), 32.1 (C-29), 50.7 (O*C*H$_3$), 63.3 (C-23), 65.1 (C-5’), 65.5 (C-5”), 69.6 (C-4”), 71.9 (C-2’), 73.0 (C-3’), 73.8 (C-2”), 76.3 (C-3”), 78.4 (C-4’), 82.0 (C-3), 104.9 (C-1’), 105.6 (C-1”), 122.3 (C-12), 143.6 (C-13), 178.6 (C-28). HRMS: $C_{41}H_{66}O_{12}Na$ calcd 773.4452; found 773.4441.

4.38. Methyl 3-*O*-[β-D-glucopyranosyl-(1→2)-α-L-arabinopyranosyl]hederagenate (5a). $[\alpha]_D$ = +39.8° (*c* 0.5, pyridine). Selected NMR data: ^{1}H NMR (CD_3OD) : δ 0.74 (s, 3H, H-24), 0.77 (s, 3H, H-26), 0.93 (s, 3H, H-29), 0.96 (s, 3H, H-30), 1.00 (s, 3H, H-25), 1.19 (s, 3H, H-27), 2.89 (dd, 1H, *J* = 13.6, *J* = 3.9 Hz, H-18), 3.23 (dd, 1H, *J* = 8.7, *J* = 7.9 Hz, H-2’’), 3.25 (t, 1H, *J* = 9.1 Hz, H-4’’), 3.28 (m, 1H, H-5’’), 3.32 (m, 1H, H-23a), 3.38 (dd, 1H, *J* = 9.0, *J* = 8.7 Hz, H-3’’), 3.54 (dd, 1H, *J* = 13.3, *J* = 3.3 Hz, H-5a’), 3.64 (s, 3H, OC*H*$_3$; m, 1H, H-3), 3.65 (m, 1H, H-6a’’), 3.67 (d, 1H, *J* =

11.2 Hz, H-23b), 3.77 (dd, 1H, J = 8.1, J = 3.1 Hz, H-3'), 3.85 (m, 1H, H-4'), 3.86 (m, 3H, H-6b'', H-5b', H-2'), 4.56 (d, 1H, J = 6.2 Hz, H-1'), 4.63 (d, 1H, J = 7.8 Hz, H-1''), 5.27 (m, 1H, H-12). ^{13}C NMR (CD_3OD) : δ 11.9 (C-24), 14.9 (C-25), 16.2 (C-26), 22.5 (C-30), 24.9 (C-2), 25.0 (C-27), 32.0 (C-29), 50.7 (O*C*H_3), 61.4 (C-6''), 63.3 (C-23), 64.1 (C-5'), 67.6 (C-4'), 70.2 (C-4''), 72.4 (C-3'), 74.5 (C-2''), 76.5 (C-3''), 76.8 (C-5''), 77.9 (C-2'), 82.2 (C-3), 103.1 (C-1'), 103.2 (C-1''), 122.3 (C-12), 143.6 (C-13), 178.6 (C-28). HRMS: $C_{42}H_{68}O_{13}Na$ calcd 803.4558; found 803.4554.

4.39. Methyl 3-*O*-[β-D-glucopyranosyl-(1→2)-β-L-arabinopyranosyl]hederagenate (6a). $[\alpha]_D$ = +72.2° (*c* 0.5, pyridine). Selected NMR data : ^{1}H NMR (CD_3OD) : δ 0.69 (s, 3H, H-24), 0.77 (s, 3H, H-26), 0.93 (s, 3H, H-29), 0.96 (s, 3H, H-30), 1.00 (s, 3H, H-25), 1.19 (s, 3H, H-27), 2.90 (dd, 1H, J = 13.8, J = 3.9 Hz, H-18), 3.27 (m, 1H, H-4''), 3.28 (m, 1H, H-2''), 3.30 (m, 1H, H-5''), 3.34 (m, 1H, H-23a), 3.38 (t, 1H, J = 8.8 Hz, H-3''), 3.50 (d, 1H, J = 11.1 Hz, H-23b), 3.60 (dd, 1H, J = 12.1, J = 1.6 Hz, H-5a'), 3.64 (s, 3H, OC*H*$_3$), 3.67 (dd, 1H, J = 11.8, J = 5.7 Hz, H-6a''), 3.72 (dd, 1H, J = 11.6, J = 4.5 Hz, H-3), 3.86 (dd, 1H, J = 9.5, J = 3.3 Hz, H-2'), 3.90 (dd, 1H, J = 11.8, J = 2.0 Hz, H-6b''), 3.94 (m, 1H, H-4'), 3.96 (dd, 1H, J = 9.7, J = 3.4 Hz, H-3'), 3.99 (brd, 1H, J = 12.0 Hz, H-5b'), 4.49 (d, 1H, J = 7.7 Hz, H-1''), 5.28 (m, 1H, H-12 ; d, 1H, J = 3.2 Hz, H-1'). ^{13}C NMR (CD_3OD) : δ 12.4 (C-24), 14.8 (C-25), 16.2 (C-26), 22.1 (C-2), 22.5 (C-30), 25.0 (C-27), 32.0 (C-29), 50.7 (O*C*H_3), 61.5 (C-6''), 63.3 (C-5'), 63.5 (C-23), 68.0 (C-3'), 69.4 (C-4'), 70.3 (C-4''), 74.2 (C-2''), 76.5 (C-3''), 76.6 (C-5''), 78.0 (C-3), 78.6 (C-2'), 97.8 (C-1'), 104.5 (C-1''), 122.4 (C-12), 143.6 (C-13), 178.6 (C-28). HRMS: $C_{42}H_{68}O_{13}Na$ calcd 803.4558; found 803.4554.

4.40. Methyl 3-*O*-[β-D-glucopyranosyl-(1→3)-α-L-arabinopyranosyl]hederagenate (7a). $[\alpha]_D$ = +47.0° (*c* 0.5, pyridine). Selected NMR data : ^{1}H NMR (CD_3OD) : δ 0.84 (s, 3H, H-24), 0.87 (s, 3H, H-26), 0.93 (s, 3H, H-29), 0.96 (s, 3H, H-30), 1.00 (s, 3H, H-25), 1.19 (s, 3H, H-27), 2.89 (dd, 1H, J = 13.5, J = 4.0 Hz, H-18), 3.30 (m, 1H, H-5''), 3.32 (m, 1H, H-2''), 3.32 (m, 1H, H-23a), 3.37 (t, 1H, J = 8.5 Hz, H-4''), 3.40 (t, 1H, J = 8.6 Hz, H-3''), 3.59 (dd, 1H, J = 12.8, J = 1.2 Hz, H-5a'), 3.64 (s, 3H, OC*H*$_3$; m, 1H, H-3), 3.65 (m, 1H, H-3' ; d, 1H, J = 11.6 Hz, H-23b), 3.71 (dd, 1H, J = 12.1, J = 5.4 Hz, H-6a''; dd, 1H, J = 9.8, J = 7.5 Hz, H-2'), 3.85 (dd, 1H, J = 11.9, J = 2.1 Hz, H-6b''), 3.88 (dd, 1H, J = 13.0, J = 2.2 Hz, H-5b'), 4.06 (m, 1H, H-4'), 4.37 (d, 1H, J = 7.4 Hz, H-1'), 4.56 (d, 1H, J = 7.7 Hz, H-1''), 5.27 (brt, 1H, J = 3.3 Hz, H-12). ^{13}C NMR (CD_3OD) : δ 11.9, (C-24), 15.0 (C-25), 16.2 (C-26), 22.5 (C-30), 24.8 (C-2), 25.0 (C-27), 32.0 (C-29), 50.7 (O*C*H_3), 60.9 (C-6''), 63.7 (C-23), 65.4 (C-5'), 68.1 (C-4'), 69.7 (C-4''), 70.6 (C-2'), 73.9 (C-2''), 76.2 (C-3''), 76.5 (C-5''), 82.0 (C-3), 82.8 (C-3'), 104.1 (C-1''), 104.7 (C-1'), 122.3 (C-12), 143.6 (C-13), 178.6 (C-28). HRMS: $C_{42}H_{68}O_{13}Na$ calcd 803.4558; found 803.4534.

4.41. Methyl 3-*O*-[β-D-glucopyranosyl-(1→4)-α-L-arabinopyranosyl]hederagenate (8a). $[\alpha]_D$ = +22.1° (*c* 0.5, pyridine). Selected NMR data : ^{1}H NMR (CD_3OD) : δ 0.73 (s, 3H, H-24), 0.77 (s, 3H, H-26), 0.93 (s, 3H, H-29), 0.96 (s, 3H, H-30), 1.00 (s, 3H, H-25), 1.19 (s, 3H, H-27), 2.89 (dd, 1H, *J* = 13.7, *J* = 3.9 Hz, H-18), 3.30 (m, 2H, H-2'', H-5''), 3.32 (m, 1H, H-23a), 3.33 (m, 1H, H-4''), 3.37 (t, 1H, *J* = 8.6 Hz, H-3''), 3.56 (m, 3H, H-2', H-3', H-5a'), 3.63 (m, 1H, H-3), 3.64 (s, 3H, OCH_3; d, 1H, *J* = 11.2 Hz, H-23b), 3.68 (dd, 1H, *J* = 12.0, *J* = 5.3 Hz, H-6a''), 3.87 (dd, 1H, *J* = 12.1, *J* = 2.1 Hz, H-6b''), 3.93 (m, 1H, H-4'), 4.20 (dd, 1H, *J* = 12.7, *J* = 2.4 Hz, H-5b'), 4.33 (d, 1H, *J* = 6.8 Hz, H-1'), 4.49 (d, 1H, *J* = 7.6 Hz, H-1''), 5.27 (m, 1H, H-12). ^{13}C NMR (CD_3OD) : δ 11.9 (C-24), 14.9 (C-25), 16.2 (C-26), 22.5 (C-30), 24.7 (C-2), 25.0 (C-27), 32.1 (C-29), 50.7 (OCH_3), 61.1 (C-6''), 63.3 (C-23), 65.1 (C-5'), 69.8 (C-4''), 71.9 (C-2'), 73.0 (C-3'), 73.9 (C-2''), 76.4 (C-3''), 76.5 (C-5''), 78.5 (C-4'), 81.9 (C-3), 104.8 (C-1'), 104.9 (C-1''), 122.3 (C-12), 143.6 (C-13), 178.6 (C-28). HRMS: $C_{42}H_{68}O_{13}Na$ calcd 803.4558; found 803.4531.

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