Synthesis of α-Hederin, δ-Hederin, and Related Triterpenoid Saponins

Karen Plé,*[a] Martin Chwalek,[a] and Laurence Voutquenne-Nazabadioko[a]

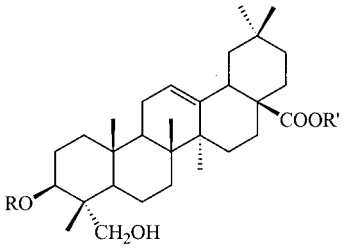
Keywords: Glycosylation / Natural products / Saponins / Total synthesis

The synthesis of α-hederin (3-*O*-[α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl]hederagenin, **1**), δ-hederin (3-*O*-(α-L-arabinopyranosyl)hederagenin, **3**), and three related triterpenoid saponins is described as part of a study of the structure–activity relationships between triterpenoid saponins and hemolytic activity. 4-Methoxybenzyl α-L-arabinopyranoside (**11**) was synthesized first and then used to prepare the different arabinose acceptors. Glycosylation between the acceptors and 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (**20**) was performed in excellent yield to give the desired disaccharides. Coupling of the trichloroacetimidate derivatives of the disaccharides to allyl- or methyl-hederagenin gave the protected saponosides in high yields. The saponins and their corresponding methyl esters were then obtained in good to moderate yields after deprotection.

Introduction

α-Hederin (3-*O*-[α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl]hederagenin, **1**), also known as kalopanaxsaponin A or sapindoside A, and δ-hederin (3-*O*-(α-L-arabinopyranosyl)hederagenin, **3**), also known as koelreuteria saponin A, are natural products (Figure 1) belonging to the family of triterpenoid saponins and are widely distributed in nature.[1] Both of these molecules possess molluscicidal[2] and cytotoxic[3] activities. In addition, α-hederin has been shown to possess antifungal and antileishmanial activities,[4] as well as in vivo antitumor activity.[5] More recently, the antiinflammatory activity of α-hederin[6] and α-hederin methyl ester[7] (**2**) has also been reported.

One of the oldest known activities of α-hederin, δ-hederin, and, in general, many saponins, is their ability to lyse red blood cells.[1,8] Our laboratory has long been interested in saponin isolation and identification, and, more recently, in the structure−activity relationships of hemolytic saponins.[9] Many saponins containing hederagenin have been shown to possess strong hemolytic activity. For example, α-hederin has a stronger activity (20 μg/mL for 100% hemolysis) than the commercial saponin from Sigma® (75 μg/mL), which is sold as a mixture of saponosides.[9] Most of the existing structure−activity relationships of hemolytic saponins have focused on the aglycon or the number of sugar units involved.[8−10] Using the activity of α-hederin as a starting point, we wished to approach the problem in a different way by restricting our study to saponins containing hederagenin, and by varying the type and position of the sugar units in relation to one another. A similar strategy was used in the synthesis of the oleanolic acid saponins Randianin and Arvensoside B.[11,12]



R = α-L-Rha-(1→2)-α-L-Ara	R' = H (α-hederin) **(1)**
	R' = CH_3 **(2)**
R = α-L-Ara	R' = H (δ-hederin) **(3)**
	R' = CH_3 **(4)**
R = α-L-Rha-(1→2)-β-L-Ara	R' = H **(5)**
	R' = CH_3 **(6)**
R = α-L-Rha-(1→3)-α-L-Ara	R' = H **(7)**
	R' = CH_3 **(8)**
R = α-L-Rha-(1→4)-α-L-Ara	R' = H **(9)**
	R' = CH_3 **(10)**

Figure 1. α-Hederin, δ-hederin and related saponins

Because saponin extraction from natural sources can be long and tedious, and results in very small quantities of the desired saponin being obtained, our goal was to synthesize naturally occurring α-hederin (**1**), δ-hederin (**3**), as well as the "non-natural" saponins 3-*O*-[α-L-rhamnopyranosyl-(1→2)-β-L-arabinopyranosyl]hederagenin (**5**), 3-*O*-[α-L-rhamnopyranosyl-(1→3)-α-L-arabinopyranosyl]hederagenin

[a] Université de Reims Champagne-Ardenne, CNRS UMR 6013, CPCBAI,
Bât 18, Moulin de la Housse, BP 1039, 51687 Reims, France
E-mail: karen.ple@univ-reims.fr

  DOI: 10.1002/ejoc.200300723

(**7**), and 3-*O*-[α-L-rhamnopyranosyl-(1→4)-α-L-arabinopyranosyl]hederagenin (**9**), and their corresponding methyl esters (Figure 1).

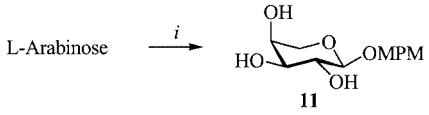
Interest in saponins is rapidly increasing because of their diverse biological properties. Of the two types of saponins present in nature, possessing either a steroid or triterpenoid aglycon, the majority of synthetic studies have focused on the former.[13] Many syntheses of triterpenoid saponins exist in the literature,[14] but those with aglycons other than oleanolic acid are not widespread.[10a,15] This situation is due, perhaps, to the small quantities of aglycon obtained from natural product extraction, which can be a limiting factor in the synthesis of these types of molecules. For this reason, and for ease of synthesis, all of the desired saponins in our study were retrosynthetically disconnected into the triterpenoid moiety and the mono- or disaccharide sugar part.

Very little work has been published concerning the preparation of rhamnose−arabinose disaccharides. The first synthesis of an α-L-rhamnopyranosyl-(1→2)-β-L-arabinopyranoside derivative was published in 1982 as part of a ^{13}C NMR spectroscopy study of methyl and benzyl β-L-arabinose oligosaccharides.[16] The desired disaccharide was synthesized using a suitably protected benzyl-β-arabinose derivative, having a free hydroxy group in position 2, and an acetylated rhamnopyranosyl bromide in the presence of an excess of mercury cyanide in 71% yield. Kamiya et al. also reported the synthesis of α-L-rhamnopyranosyl-(1→2)-L-arabinopyranoside in 1984,[17] as part of a study to investigate the substrate specificity of α-L-rhamnosidase induced in *Aspergillus niger*. The protected disaccharide was synthesized in only 38% yield, again using an acetylated rhamnopyranosyl bromide as the donor. The same group then published the synthesis of methyl α-L-rhamnopyranosyl-(1→4)-β-L-arabinopyranoside in 1985.[18] This compound was synthesized from benzoylated rhamnopyranosyl bromide in 7% yield after debenzoylation and peracetylation of the resulting disaccharide. Finally, the synthesis of benzyl α-L-rhamnopyranosyl-(1→3)-β-L-arabinopyranoside followed in 1986;[19] this derivative was synthesized via an acetylated rhamnopyranosyl chloride in 70% yield.

We report here the first synthesis of the biologically active saponins α-hederin and δ-hederin, related triterpenoid saponins, and their methyl esters. We have developed a highly improved method for the preparation of the rhamnose−arabinose disaccharides and we have performed the coupling of these disaccharides to methyl or allyl hederagenate in high yields. Total deprotection then affords the desired saponins in good to moderate yields.

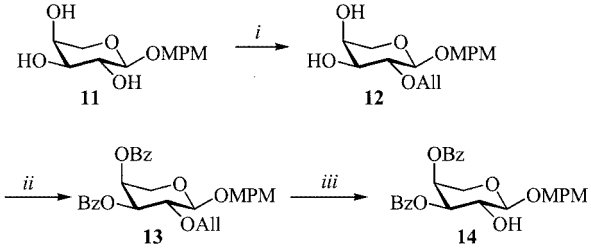
Results and Discussion

The starting point of our monosaccharide synthesis was the preparation of three suitably protected arabinose derivatives ready for coupling in positions 2, 3, and 4. The protecting group in the anomeric position of arabinose had to be chosen carefully so that a unique starting material would give access to all three compounds. Because the allyl group is not compatible with the series of steps envisioned to prepare the desired molecules, and the benzyl group proved difficult to deprotect, we considered the 4-methoxybenzyl (MPM) group. Although the use of this protecting group is widespread in oligosaccharide synthesis, protection in the anomeric position of sugars has, until now, been limited to monosaccharides in the hexose family[20] and a few disaccharide derivatives.[21] The new 4-methoxybenzyl α-L-arabinopyranoside (**11**) was synthesized readily from L-arabinose in four steps and 51% global yield without intermediate purification (Scheme 1).



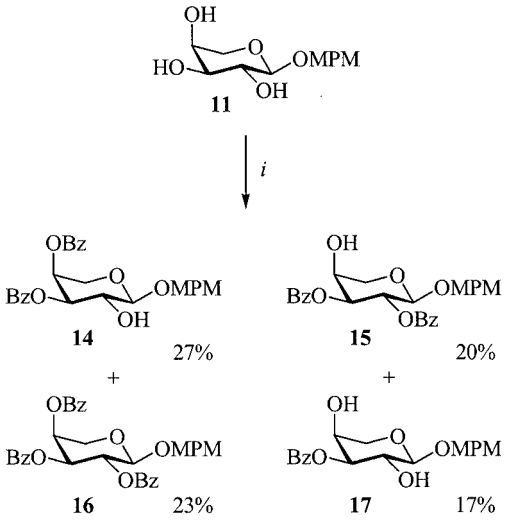
Scheme 1. Reagents and reaction conditions: (*i*) a) Ac_2O, pyridine; b) 33% HBr/AcOH; c) *p*-methoxybenzyl alcohol, I_2, Ag_2CO_3; d) Et_3N, MeOH, H_2O (51%, 4 steps)

This compound then served as the starting material for monosaccharide elaboration. We began the synthesis of the arabinose derivative **14** having a free hydroxy group in position 2 by selective protection of the hydroxy groups in position 3 and 4 of **11** with 2,2-dimethoxypropane, allylation in position 2, and then removal of the acetonide to give compound **12** in 73% yield over three steps. The free hydroxy groups were then benzoylated to give **13**, and the allyl group was removed to give the desired compound **14** (Scheme 2).



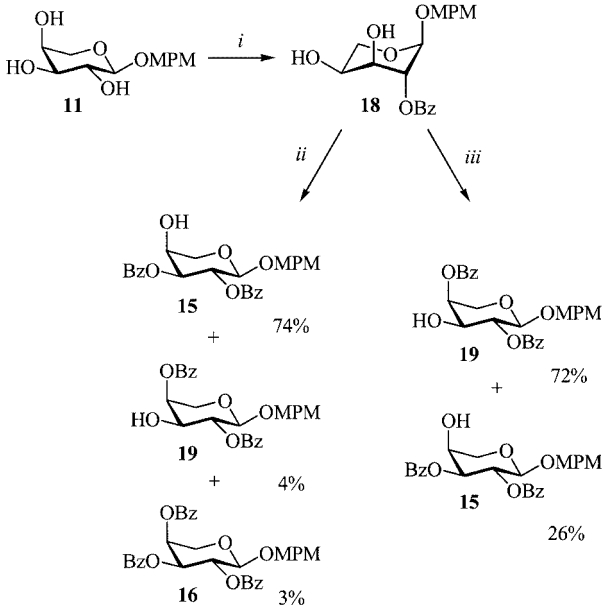
Scheme 2. Reagents and reaction conditions: (*i*) a) 2,2-dimethoxypropane, TsOH, DMF; b) NaH, allyl bromide, DMF; c) 70% AcOH, 70 °C (73%, 3 steps); (*ii*) benzoyl chloride, Et_3N, DMAP (87%); (*iii*) $PdCl_2$/MeOH (68%)

Initially, we believed that the synthesis of the arabinose derivative **15** having a free hydroxy group in position 4 would be possible by selective benzoylation of compound **11** at low temperature in pyridine.[22] Previously, selective benzoylation of allyl β-L-arabinopyranoside at −40 °C in our laboratory (unpublished results) gave the 2,3-di-*O*-benzoylated product preferentially. When this same reaction was applied to the α-MPM derivative **11**, the reaction was much less selective and give a range of all possible benzoylated products (Scheme 3).



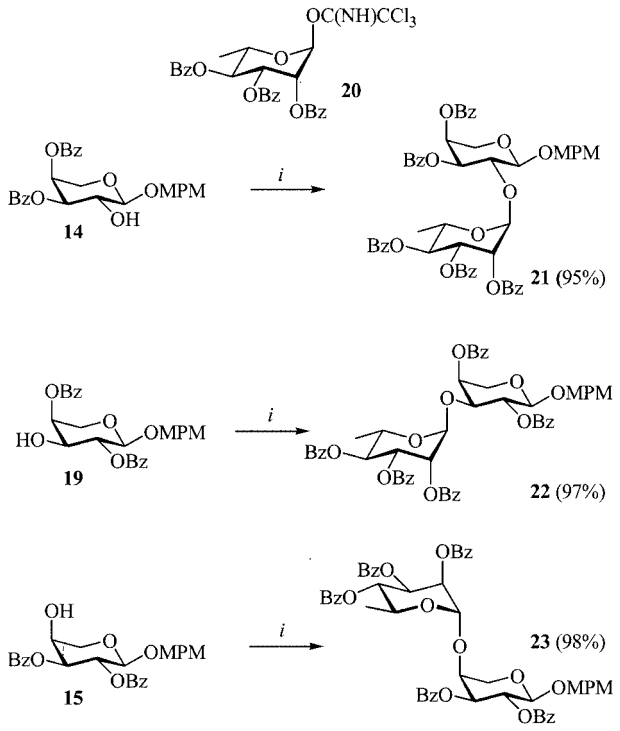
Scheme 3. Reagents and reaction conditions: (*i*) benzoyl chloride (2.1 equiv.), pyridine, −40 °C

We believe that the outcome of the reaction is a direct result of the MPM group being in the equatorial position rather than the axial one. Based on the reaction products, 3-*O*-benzoylation occurred first; the mono-benzoylated compound **17** was isolated in 17% yield. The resulting steric interaction between a second benzoyl group in position 2 and the anomeric MPM group on one side and the 3-*O*-benzoyl group on the other then influences the reaction's selectivity. Competition between ester formation in positions 2 or 4 is equal, and, in this case, the axial position is favored as the 3,4-di-*O*-benzoylated compound **14** was isolated as the *major* reaction product.

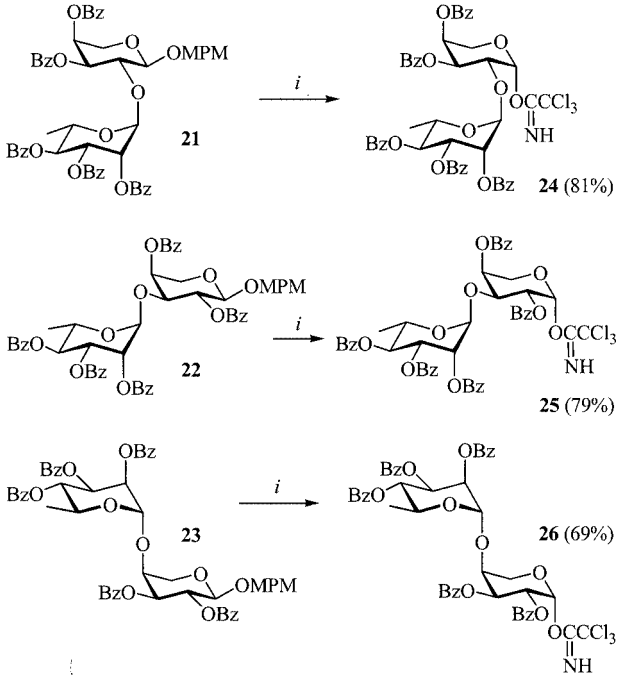


Scheme 4. Reagents and reaction conditions: (*i*) a) 2,2-dimethoxypropane, TsOH, DMF; b) benzoyl chloride, Et_3N, DMAP; c) 70% AcOH, 70 °C (80%, 3 steps); (*ii*) benzoyl chloride (1.1 equiv.), pyridine, −35 °C; (*iii*) a) $PhC(OCH_3)_3$, TsOH; b) 90% AcOH

To circumvent this problem, compound **18**, which is benzoylated in position 2, was prepared from **11** in good yield (80% over three steps). It is interesting to note that the arabinose derivative **18** is no longer in the common $^4C_1$ configuration: the six-membered ring "flips" to relieve steric



Scheme 5. Reagents and reaction conditions: (*i*) trichloroacetimidate **20**, CH_2Cl_2, TMSOTF (0.05 equiv.), 4-A molecular sieves, −20 °C

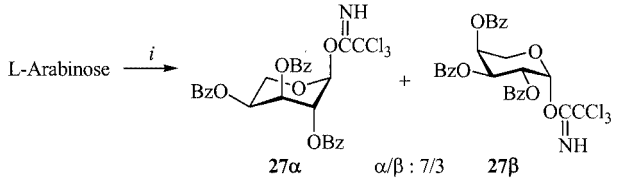


Scheme 6. Reagents and reaction conditions: (*i*) a) TFA, H_2O; b) CCl_3CN, DBU

hindrance. Selective benzoylation at −35 °C gave 74% of the desired product **15** as well as very small amounts of the 2,4-di-*O*-benzoylated (4%) and tribenzoylated (3%) arabinose derivatives (**19** and **16**, respectively; Scheme 4).

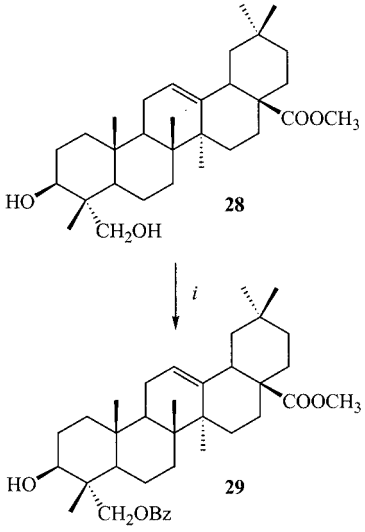
Compound **18** also served as a common intermediate in the synthesis of the arabinose derivative having a free hydroxy group in position 3. Treatment with trimethyl orthobenzoate, followed by acid-catalyzed opening of the orthoester, gave the desired product **19** in 72% yield, as well as 26% of the 2,3-di-*O*-benzoylated derivative **15** (Scheme 4).

Lewis acid-catalyzed assembly of the acceptors **14**, **15**, and **19** and the donor 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (**20**)[23] by trimethylsilyl trifluoromethanesulfonate (TMSOTf)[24] was straightforward and high yielding to give the disaccharides **21**, **22**, and **23** (Scheme 5). The choice of a benzoylated rhamnose derivative was essential for avoiding orthoester formation and increasing reaction yields.

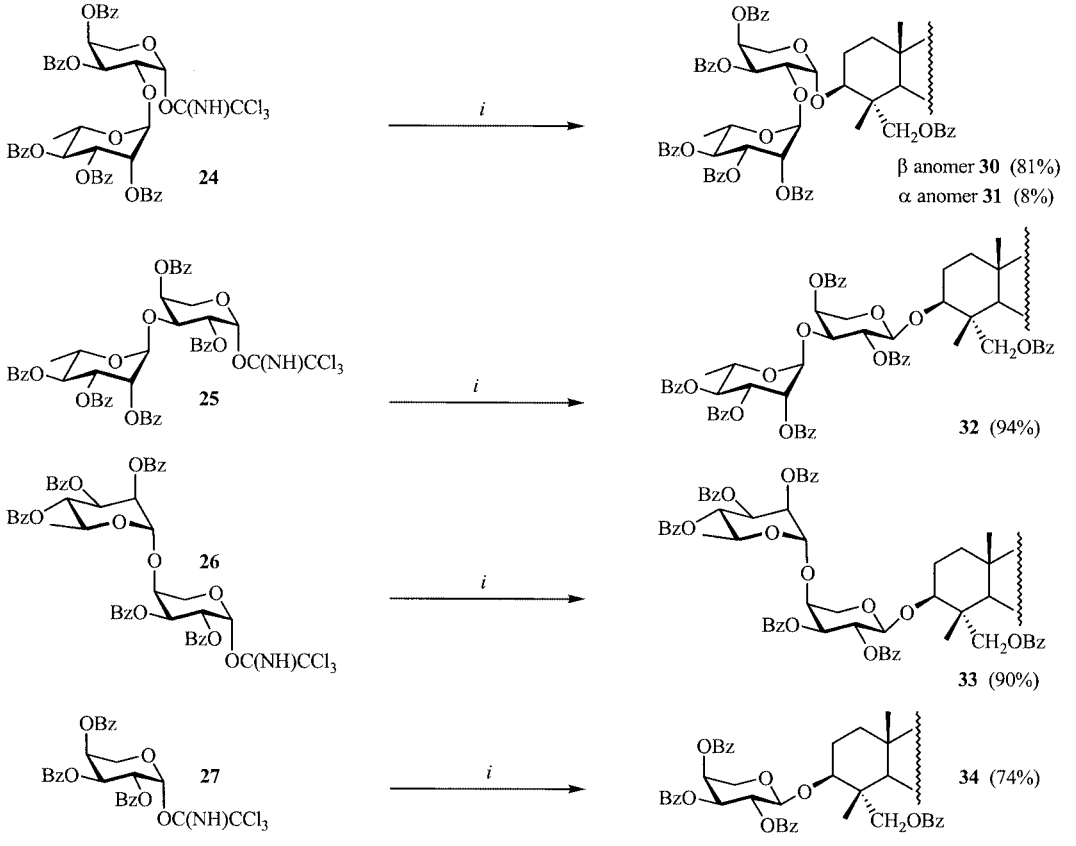


Scheme 7. Reagents and reaction conditions: (*i*) a) benzoyl chloride, pyridine; b) 33% HBr/AcOH; c) NaI/H_2O; d) CCl_3CN, DBU, 4 h, 25 °C (77%, 4 steps)

The anomeric MPM group was then hydrolyzed with trifluoromethanesulfonic acid (TFA) and the resulting hemiacetal was then treated with trichloroacetonitrile and catalytic 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to form the trichloroacetimidates **24**, **25**, and **26** in 81, 79, and 69% yields, respectively (Scheme 6).



Scheme 8. Reagents and reaction conditions: *i*) benzoyl chloride, pyridine, room temp. (71%)



Scheme 9. Reagents and reaction conditions: (*i*) alcohol **29**, TMSOTf (0.05 equiv.), 4-Å molecular sieves, CH_2Cl_2, −20 °C

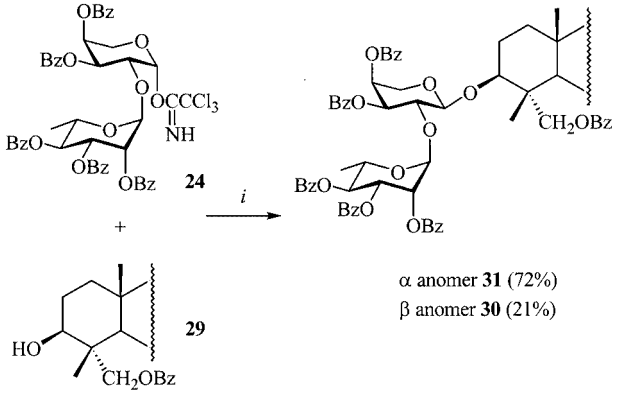
The use of 2,3,4-tri-*O*-benzoyl-β-L-arabinose trichloroacetimidate (**27**) was also necessary for the δ-hederin synthesis; it was readily prepared from L-arabinose. Perbenzoylation, bromination in the anomeric position with HBr/AcOH, hydrolysis of the bromide by sodium iodide in the presence of H_2O, and then reaction with trichloroacetonitrile gave the desired product in 77% yield over 4 steps (Scheme 7).

It is interesting to note that a short reaction time for trichloroacetimidate formation leads to a mixture of α and β products in the $^1C_4$ and $^4C_1$ configurations, respectively. Leaving the reaction overnight favors the thermodynamically more stable β anomer and facilitates purification.

With the various trichloroacetimidates in hand, the last step was the preparation of the suitably protected triterpenoid derivative. To have access to both the saponin methyl ester and the saponin, we chose methyl hederagenate **28** to be the starting material. Selective protection of the primary alcohol was accomplished by treatment with 1.4 equivalents of benzoyl chloride at room temperature to give the mono-protected derivative **29** in 71% yield (Scheme 8).

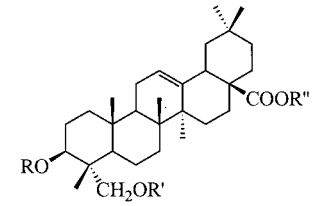
Saponin synthesis proceeded smoothly by reacting the prepared trichloroacetimidates **25**, **26**, and **27** and the acceptor **29** at −20 °C in the presence of catalytic amounts of TMSOTf. As expected, the α anomers were formed exclusively in good to excellent yields. Glycosylation of donor **24** with acceptor **29** gave, because of the presence of rhamnose in position 2, 81% of the β anomer (**30**) along with 8% of the α anomer (**31**). This result was expected, because we wished to synthesize, and later test, the "non-natural" saponin that has the opposite anomeric configuration of α-hederin between the disaccharide and the aglycon (Scheme 9).

Glycosylation that results in the formation of an equatorial bond between an aglycon and a disaccharide lacking a participating ester group in position 2 is not a trivial matter. Many literature examples of saponin synthesis involve stepwise construction of the disaccharide, i.e., glycosylation of the aglycon with a monosaccharide protected in position 2 by an ester function, deprotection of the ester, and then coupling of a second sugar unit. We chose not to apply this strategy to the synthesis of α-hederin in an effort to avoid substantial protecting group manipulation. To prepare the protected α-hederin derivative **31** in good yield, the coupling reaction was carried out in propionitrile, which is known to promote equatorial bond formation in glycoside synthesis when neighboring group participation is nonexistent.[25] Glycosylation at −78 °C with 0.3 equiv. of TMSOTf gave 72% of the desired saponin **31** along with 21% of the β anomer **30** (Scheme 10).

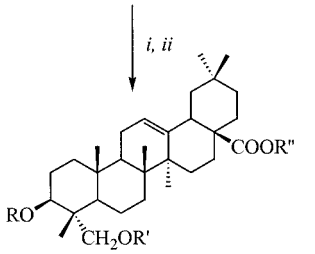


Scheme 10. Reagents and reaction conditions: (*i*) TMSOTf (0.3 equiv.), 4-Å molecular sieves, propionitrile, −78 °C

Total deprotection of the saponins proceeded in two steps. First, removal of the benzoate esters with 3% potassium hydroxide in CH_3OH gave the saponin methyl esters in good to excellent yields. Deprotection of the methyl ester proved difficult. Traditional saponification methods (5% KOH/CH_3OH, 65 °C, several days; barium hydroxide/CH_3OH/H_2O, reflux) failed. Halogenolysis with lithium iodide in DMF[26] gave the saponins in poor yields (Scheme 11) because of the drastic reaction conditions and the difficulties encountered during product purification (as an aqueous workup was not possible).



R = benzoylated mono or disaccharides



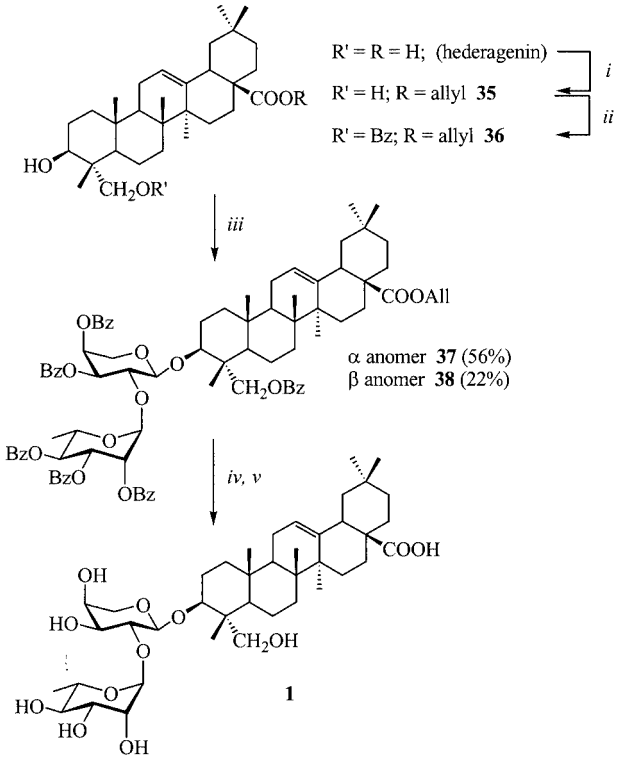
R = deprotected mono or disaccharides

R' = Bz, R" = CH_3	*i*	R' = H, R" = CH_3	*ii*	R' = H, R" = H
31		**2** (75%)		**1** (48%)
30		**6** (90%)		**5** (46%)
32		**8** (87%)		**7** (31%)
33		**10** (96%)		**9** (47%)
34		**4** (93%)		**3** (20%)

Scheme 11. Reagents and reaction conditions: (*i*) 3% KOH/CH_3OH; (*ii*) LiI, DMF, reflux, 5 d

This problem was eliminated by using an allyl ester protecting group. Glycosylation using allyl hederagenate **35** gave the protected saponins in yields identical to those obtained with the methyl esters.[27] Total deprotection (debenzoylation and palladium-catalyzed ester removal) was then performed without intermediate purification to give the corresponding saponins. For example, compound **37**, the protected α-hederin derivative, was synthesized in 56% yield using the same reaction conditions as shown in Scheme 10.

Two-step deprotection, without purification of the intermediate, gave α-hederin (**1**) in 91% yield, which is a net improvement over the yield obtained in the case of the methyl ester (36%) (Scheme 12).



Scheme 12. Reagents and reaction conditions: (*i*) allyl bromide, K_2CO_3, DMF, 50 °C (61%); (*ii*) benzoyl chloride, pyridine, room temp. (63%); (*iii*) trichloroacetimidate **24**, TMSOTf (0.3 equiv.), 4-Å molecular sieves, propionitrile, −78 °C; (*iv*) 3% KOH/MeOH; (*v*) [$Pd(PPh_3)_4$], pyrrolidine, THF (91%, 2 steps)

Using the allyl ester **35** resulted in a significant yield increase for all of the saponins. Table 1 summarizes the yields obtained for the last three synthetic steps: glycosylation, debenzoylation, and ester deprotection for the two aglycons used.

Table 1. Comparative overall yields for saponin glycosylation and deprotection

	Methyl hederagenate	Allyl hederagenate
α-L-Rha-(1→2)-α-L-Ara (**1**)	26%	51%
α-L-Rha-(1→2)-β-L-Ara (**5**)	34%	64%
α-L-Rha-(1→3)-α-L-Ara (**7**)	25%	79%
α-L-Rha-(1→4)-α-L-Ara (**9**)	41%	76%
α-L-Ara (**3**)	14%	74%

In conclusion, we have synthesized the naturally occurring saponins α-hederin (**1**) and δ-hederin (**3**), as well as the "non-natural" saponins **5**, **7**, and **9**, in a clear and straightforward manner in yields ranging from 54 to 86% for the saponin methyl esters, and 51−79% for the saponins. The saponin syntheses developed here give access to products which are not abundant or readily isolated from natural sources.

The use of 4-methoxybenzyl α-L-arabinopyranoside (**11**) gave ready access to the desired arabinose derivatives with minimal protecting group manipulation. This synthesis of the rhamnose−arabinose disaccharides is a great improvement over previous methods, and the coupling to the aglycon was achieved in excellent yields. Work is currently underway to test the hemolytic activity of these molecules and the preparation of other hederagenin containing saponins is also in progress.

Experimental Section

General Remarks: All chemicals were reagent grade and used as supplied unless otherwise noted. Dichloromethane (CH_2Cl_2) and triethylamine were heated under reflux over calcium hydride and distilled prior to use. All reactions were performed under Ar 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 a solution of anisaldehyde in ethanol and then heating. Column chromatography was performed using E. Merck Geduran Silica Gel Si 60 (40−60 μM). Optical rotations were recorded at 21 °C using a Perkin−Elmer 241 polarimeter. ESI-MS were recorded using a Thermofinnigan quadripolar mass spectrometer with positive ion data collected automatically. 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 with a Perkin−Elmer CHN 2400. Methyl hederagenate (**28**)[28] was obtained from an ivy plant extract[29] (*Hedera taurica*, Araliaceae), which was enriched in hederasaponin C, by acidic hydrolysis and treatment with diazomethane. 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-Methoxybenzyl α-L-Arabinopyranoside (11): Acetic anhydride (Ac_2O; 44 mL, 466 mmol, 5 equiv.) was slowly added to a solution of L-arabinose (14.0 g, 93 mmol) and pyridine (75.4 mL, 933 mmol, 10 equiv.) at 0 °C. After 48 h, toluene was added (3 ×) and the solvent evaporated under reduced pressure until an oil was obtained (35 g). A solution of 33% HBr in AcOH (50 mL) was then added. After 2 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 (200 mL) and poured into ice water (200 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 150 mL). The combined organic layers were then washed with H_2O (2 × 250 mL), satd. $NaHCO_3$ (250 mL), and satd. NaCl (250 mL). The dried solution (Na_2SO_4) was evaporated under reduced pressure until formation of a white solid just began. Diethyl ether (50 mL) was added and the product was left to precipitate for 30 min. The solid was filtered and dried to give the bromide (21.7 g, 68%).

The bromide (19.9 g, 59 mmol) was then mixed with toluene (250 mL) and 4-Å molecular sieves (44 g) for 40 min before adding 4-methoxybenzyl alcohol (37 mL, 294 mmol, 5 equiv.), I_2 (22.3 g, 88.1 mmol, 1.5 equiv.), and Ag_2CO_3 (32.4 g, 117 mmol, 2 equiv.). After stirring overnight, the reaction mixture was filtered through celite and the pad was washed with toluene. The organic layer was then washed with 20% $Na_2S_2O_3$ (500 mL), H_2O (500 mL), and satd. NaCl (500 mL). The dried solution (Na_2SO_4) was then evaporated under reduced pressure to give an oil (49.8 g) that was stirred

overnight in a mixture of MeOH/Et_3N/H_2O (8:1:1, 600 mL). The reaction mixture was evaporated under reduced pressure and the crude residue (45.9 g) was purified by column chromatography (EtOAc then EtOAc/MeOH, 9:1) to give **11** as a white solid (11.9 g, 75%; 51% global yield from L-arabinose). R_f = 0.34 (EtOAc/MeOH, 9:1). M.p. 107−109 °C. $[\alpha]_D$ = −26.1 (*c* = 1, CH_3OH). ^1H NMR (CD_3OD): δ = 3.53 (dd, $J_{2,3}$ = 8.9, $J_{3,4}$ = 3.4 Hz, 1 H, H-3), 3.56 (dd, $J_{5a,5b}$ = 12.5, $J_{4,5a}$ = 1.6 Hz, 1 H, H-5a), 3.61 (dd, $J_{2,3}$ = 8.8, $J_{1,2}$ = 7.0 Hz, 1 H, H-2), 3.80 (s, 3 H, OC*H*$_3$), 3.82 (m, 1 H, H-4), 3.93 (dd, $J_{5a,5b}$ = 12.5, $J_{4,5b}$ = 3.1 Hz, 1 H, H-5b), 4.29 (d, $J_{1,2}$ = 7.0 Hz, 1 H, H-1), 4.56 (d, *J* = 11.3 Hz, 1 H, C*H*$_2$MPM), 4.80 (d, *J* = 11.3 Hz, 1 H, C*H*$_2$MPM), 6.90 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.34 (d, *J* = 8.7 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (CD_3OD): δ = 54.2 (O*C*H$_3$), 65.3 (C-5), 68.1 (C-4), 69.8 (*C*H$_2$MPM), 70.9 (C-2), 72.8 (C-3), 102.0 (C-1), 113.2 (CH), 129.4 (CH), 129.5 (C), 159.4 (C) ppm. ESI-MS: *m*/*z* = 293 $[M + Na]^+$. $C_{13}H_{18}O_6$ (270.28): calcd. C 57.77, H 6.71; found C 57.62, H 6.91.

4-Methoxybenzyl 2-*O*-Allyl-α-L-arabinopyranoside (12): A solution of **11** (11 g, 40.7 mmol), 2,2-dimethoxypropane (10 mL, 81.4 mmol, 2 equiv.), and *p*-toluenesulfonic acid (0.387 g, 2.0 mmol, 0.05 equiv.) in DMF (80 mL) was stirred for 2 h at room temperature. The reaction was stopped by the addition of triethylamine (2.2 mL) and then the mixture was diluted with diethyl ether (300 mL) and washed with H_2O (250 mL). The aqueous layer was extracted with diethyl ether (4 × 250 mL). The combined organic layers were washed with satd. $NaHCO_3$ (800 mL) and satd. NaCl (800 mL). The dried solution (Na_2SO_4) was then evaporated under reduced pressure to give *p*-methoxybenzyl 3,4-*O*-isopropylidene-α-L-arabinopyranoside (12.3 g), which was used without purification in the following step.

A mixture of this isopropylidene (5.3 g, 17.1 mmol) and allyl bromide (1.8 mL, 20.5 mmol, 1.2 equiv.) in DMF (53 mL) was added to a solution of NaH (80%; 1.076 g, 35.9 mmol, 2.1 equiv.) in DMF (27 mL) at 0 °C. The reaction mixture was stirred for 1 h, quenched by the addition of MeOH, diluted in diethyl ether (250 mL), and washed with H_2O (400 mL). The aqueous layer was extracted with diethyl ether (3 × 250 mL). The combined organic layers were washed with satd. $NaHCO_3$ (600 mL) and satd. NaCl (600 mL). The dried solution (Na_2SO_4) was evaporated under reduced pressure to give an orange oil (6.4 g), which was then mixed with 70% AcOH (71.5 mL) and heated to 70 °C for 1 h. The reaction mixture was cooled and the solvent evaporated under reduced pressure in the presence of toluene (3 ×), MeOH (2 ×), and CH_2Cl_2 (2 ×) to give a yellow amorphous solid that was purified by column chromatography (cyclohexane/EtOAc, 4:6 to 2:8) to give **12** as a white solid (3.9 g, 73%). R_f = 0.20 (cyclohexane/EtOAc, 6:4). M.p. 74 °C. $[\alpha]_D$ = −40.1 (*c* = 1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 3.57 (dd, $J_{2,3}$ = 6.1, $J_{1,2}$ = 4.5 Hz, 1 H, H-2), 3.63 (dd, $J_{5a,5b}$ = 12.0, $J_{4,5a}$ = 3.7 Hz, 1 H, H-5a), 3.81 (dd, $J_{5a,5b}$ = 12.2, $J_{4,5b}$ = 6.7 Hz, 1 H, H-5b), 3.81 (m, 1 H, H-3), 3.83 (s, 3 H, OC*H*$_3$), 3.97 (td, $J_{3,4}$ = $J_{4,5a}$ = 6.9, $J_{4,5e}$ = 3.5 Hz, 1 H, H-4), 4.12 (dd, *J* = 12.7, *J* = 5.8 Hz, 1 H, C*H*$_2$CH=CH$_2$), 4.24 (dd, *J* = 12.7, *J* = 5.8 Hz, 1 H, C*H*$_2$CH=CH$_2$), 4.52 (d, *J* = 11.4 Hz, 1 H, C*H*$_2$MPM), 4.61 (d, $J_{1,2}$ = 4.3 Hz, 1 H, H-1), 4.79 (d, *J* = 11.4 Hz, 1 H, C*H*$_2$MPM), 5.21 (d, *J* = 10.3 Hz, 1 H, CH$_2$CH=C*H*$_2$), 5.28 (dd, *J* = 17.2, *J* = 1.5 Hz, 1 H, CH$_2$CH=C*H*$_2$), 5.90 (m, 1 H, CH$_2$C*H*=CH$_2$), 6.91 (d, *J* = 8.6 Hz, 2 H, Ar-H), 7.29 (m, *J* = 8.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.2 (O*C*H$_3$), 62.1 (C-5), 65.8 (C-4), 69.8 (*C*H$_2$MPM), 70.4 (C-3), 72.4 (*C*H$_2$CH=CH$_2$), 76.9 (C-2), 99.1 (C-1), 113.9 (CH), 117.7 (CH$_2$CH=*C*H$_2$), 128.7 (C), 129.7 (CH), 134.3 (CH$_2$*C*H=CH$_2$), 159.4 (C) ppm. ESI-MS: *m*/*z* = 333 $[M + Na]^+$. $C_{16}H_{22}O_6$ (310.35): calcd. C 61.92, H 7.15; found C 62.23, H 6.95.

4-Methoxybenzyl 2-*O*-Allyl-3,4-di-*O*-benzoyl-α-L-arabinopyranoside (13): Benzoyl chloride (3.0 mL, 25.5 mmol, 2.2 equiv.) was slowly added to a mixture of compound **12** (3.6 g, 11.6 mmol), triethylamine (8.1 mL, 58 mmol, 5.0 equiv.), and dimethylaminopyridine (DMAP; 0.142 g, 1.2 mmol, 0.1 equiv.) in anhydrous CH_2Cl_2 (134 mL) at 0 °C. The reaction mixture was stirred for 24 h at room temperature and quenched by the addition of MeOH. The reaction mixture was diluted with CH_2Cl_2 (300 mL) and washed with 1 M HCl (300 mL), satd. $NaHCO_3$ (300 mL), and satd. NaCl (300 mL). The dried solution (Na_2SO_4) was then evaporated under reduced pressure to give an orange oil that was recrystallized from MeOH (70 mL) to give compound **13** as white crystals (4.5 g, 74%). The rest of the crude product was purified by column chromatography (cyclohexane/EtOAc, 95:5) to give an additional amount of **13** (0.767 g, 13%). Total yield: 87%. R_f = 0.58 (cyclohexane/EtOAc, 6:4). M.p. 72 °C. $[\alpha]_D$ = +81.8 (*c* = 1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 3.86 (dd, $J_{5a,5b}$ = 12.4, $J_{4,5a}$ = 2.2 Hz, 1 H, H-5a), 3.87 (s, 3 H, OC*H*$_3$), 3.92 (dd, $J_{2,3}$ = 8.2, $J_{1,2}$ = 5.9 Hz, 1 H, H-2), 4.25 (ddt, *J* = 12.6, 6.0, 1.4 Hz, 1 H, C*H*$_2$CH=CH$_2$), 4.30 (dd, $J_{5a,5b}$ = 12.6, $J_{4,5b}$ = 4.4 Hz, 1 H, H-5b), 4.37 (ddt, *J* = 12.7, 5.5, 1.4 Hz, 1 H, C*H*$_2$CH=CH$_2$), 4.66 (d, *J* = 11.3 Hz, 1 H, C*H*$_2$MPM), 4.72 (d, $J_{1,2}$ = 5.9 Hz, 1 H, H-1), 4.93 (d, *J* = 11.3 Hz, 1 H, C*H*$_2$MPM), 5.16 (ddd, *J* = 10.3, 2.8, 1.1 Hz, 1 H, CH$_2$CH=C*H*$_2$), 5.28 (ddd, *J* = 17.2, 3.2, 1.7 Hz, 1 H, CH$_2$CH=C*H*$_2$), 5.48 (dd, $J_{2,3}$ = 8.2, $J_{3,4}$ = 3.5 Hz, 1 H, H-3), 5.63 (td, $J_{3,4}$ = $J_{4,5a}$ = 4.2, $J_{4,5e}$ = 2.3 Hz, 1 H, H-4), 5.85 (m, 1 H, CH$_2$C*H*=CH$_2$), 6.92 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.36 (t, *J* = 9.2 Hz, 4 H, Ar-H), 7.45 (t, *J* = 8.0 Hz, 2 H, Ar-H), 7.54 (t, *J* = 7.5 Hz, 2 H, Ar-H), 7.59 (t, *J* = 8.6 Hz, 2 H, Ar-H), 7.96 (d, *J* = 8.4 Hz, 2 H, Ar-H), 8.04 (d, *J* = 8.4 Hz, 2 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.2 (O*C*H$_3$), 62.1 (C-5), 68.5 (C-4), 70.6 (*C*H$_2$MPM), 71.2 (C-3), 73.2 (*C*H$_2$CH=CH$_2$), 76.2 (C-2), 101.3 (C-1), 113.8 (CH), 117.3 (CH$_2$CH=*C*H$_2$), 128.3 (CH), 128.4 (CH), 129.2 (C), 129.6 (CH), 129.7 (CH), 129.8 (CH), 133.0 (CH), 133.2 (CH), 134.5 (CH$_2$*C*H=CH$_2$), 159.3 (C), 165.6 (CO), 165.6 (CO) ppm. ESI-MS: *m*/*z* = 541 $[M + Na]^+$. $C_{30}H_{30}O_8$ (518.56): calcd. C 69.49, H 5.83; found C 69.69, H 5.74.

4-Methoxybenzyl 3,4-Di-*O*-benzoyl-α-L-arabinopyranoside (14): Palladium chloride (0.53 g, 0.3 mmol, 0.3 equiv.) was added to a solution of compound **13** (5.1 g, 9.9 mmol) in MeOH (52 mL) and the reaction mixture was stirred for 48 h at room temperature. The mixture was then filtered through Celite, the solvent was evaporated under reduced pressure, and the residue purified by column chromatography (cyclohexane/EtOAc, 8:2) to give **14** as a white solid (3.2 g, 68%). R_f = 0.42 (cyclohexane/EtOAc, 6:4). M.p. 134 °C. $[\alpha]_D$ = +82.7 (*c* = 1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 3.84 (s, 3 H, OC*H*$_3$), 3.85 (dd, $J_{5a,5b}$ = 13.2, $J_{4,5a}$ = 1.2 Hz, 1 H, H-5a), 4.19 (dd, $J_{2,3}$ = 9.5, $J_{1,2}$ = 7.3 Hz, 1 H, H-2), 4.30 (dd, $J_{5a,5b}$ = 13.2, $J_{4,5b}$ = 2.7 Hz, 1 H, H-5b), 4.54 (d, $J_{1,2}$ = 7.1 Hz, 1 H, H-1), 4.66 (d, *J* = 11.2 Hz, 1 H, C*H*$_2$MPM), 4.95 (d, *J* = 11.2 Hz, 1 H, C*H*$_2$MPM), 5.38 (dd, $J_{2,3}$ = 9.6, $J_{3,4}$ = 3.6 Hz, 1 H, H-3), 5.63 (m, 1 H, H-4), 6.93 (d, *J* = 8.6 Hz, 2 H, Ar-H), 7.35 (m, 4 H, Ar-H), 7.47 (t, *J* = 7.6 Hz, 2 H, Ar-H), 7.52 (t, *J* = 7.4 Hz, 1 H, Ar-H), 7.60 (t, *J* = 7.4 Hz, 1 H, Ar-H), 7.94 (d, *J* = 8.4 Hz, 2 H, Ar-H), 8.08 (d, *J* = 8.4 Hz, 2 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.3 (O*C*H$_3$), 64.0 (C-5), 69.0 (C-4), 69.9 (C-2), 70.9 (*C*H$_2$MPM), 72.6 (C-3), 101.9 (C-1), 114.0 (CH), 128.3 (CH), 128.4 (CH), 128.7 (C), 129.4 (C), 129.6 (C), 129.8 (CH), 129.8 (CH), 129.9 (CH), 133.1 (CH), 133.3 (CH), 159.5 (C), 165.7 (CO), 165.9 (CO) ppm. ESI-MS: *m*/*z* = 479 $[M + H]^+$. $C_{27}H_{26}O_8$ (478.50): calcd. C 67.77, H 5.48; found C 67.66, H 5.53.

4-Methoxybenzyl 2-*O*-Benzoyl-α-L-arabinopyranoside (18): This compound was synthesized using *p*-methoxybenzyl 3,4-*O*-isopro-

pylidene-α-L-arabinopyranoside, which was previously described in the preparation of compound **12**. Benzoyl chloride (2.8 mL, 23.8 mmol, 1.1 equiv.) was slowly added to a mixture of the isopropylidene arabinose (6.7 g, 21.6 mmol), triethylamine (7.5 mL, 54.0 mmol, 2.5 equiv.), and DMAP (0.132 g, 1.1 mmol, 0.05 equiv.) in anhydrous CH_2Cl_2 (200 mL) at 0 °C. The reaction mixture was stirred for 24 h at room temperature and then quenched by the addition of MeOH. The reaction mixture was diluted with CH_2Cl_2 (500 mL) and washed with 1 M HCl (400 mL), satd. $NaHCO_3$ (400 mL), and satd. NaCl (400 mL). The dried solution (Na_2SO_4) was then evaporated under reduced pressure to give an orange solid (9.2 g). The crude compound was then treated with 70% AcOH (145 mL) and heated to 70 °C for 1 h. The reaction mixture was cooled and then the solvent was evaporated under reduced pressure in the presence of toluene (3 ×), MeOH (2 ×), and CH_2Cl_2 (2 ×) to give a yellow solid (8.1 g). A first recrystallization from MeOH (80 mL) gave pure **18** (4.7 g, 59%). A second batch of crystals was obtained (1.2 g, 14%), and the rest of the crude residue was purified by column chromatography (cyclohexane/EtOAc, 1:1) to give an additional amount of **18** (0.590 g, 7%). Total yield: 80%. R_f = 0.21 (cyclohexane/EtOAc, 6:4). M.p. 143−145 °C. $[\alpha]_D$ = −49.7 (c = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 2.56 (d, J = 8.7 Hz, 1 H, OH-4), 3.48 (d, J = 9.0 Hz, 1 H, OH-3), 3.74 (dd, $J_{5a,5b}$ = 11.9, $J_{4,5a}$ = 4.2 Hz, 1 H, H-5a), 3.83 (s, 3 H, OCH_3), 3.86 (dd, $J_{5a,5b}$ = 11.9, $J_{4,5b}$ = 8.2 Hz, 1 H, H-5b), 3.99 (m, 1 H, H-3), 4.04 (m, 1 H, H-4), 4.57 (d, J = 11.6 Hz, 1 H, CH_2MPM), 4.78 (d, J = 11.6 Hz, 1 H, CH_2MPM), 4.83 (d, $J_{1,2}$ = 3.4 Hz, 1 H, H-1), 5.26 (dd, $J_{2,3}$ = 5.1, $J_{1,2}$ = 3.7 Hz, 1 H, H-2), 6.89 (d, J = 8.5 Hz, 2 H, Ar-H), 7.28 (d, J = 7.8 Hz, 2 H, Ar-H), 7.48 (t, J = 7.8 Hz, 2 H, Ar-H), 7.62 (t, J = 7.5 Hz, 1 H, Ar-H), 8.03 (d, J = 8.1 Hz, 2 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.2 (OCH$_3$), 60.9 (C-5), 65.3 (C-4), 69.6 (CH$_2$MPM), 69.7 (C-3), 71.4 (C-2), 96.5 (C-1), 113.9 (CH), 128.2 (C), 128.4 (CH), 129.1 (C), 129.8 (CH), 129.9 (CH), 133.5 (CH), 159.6 (C), 165.7 (CO) ppm. ESI-MS: m/z = 393 [M + H_2O+H]$^+$. $C_{20}H_{22}O_7$ (374.39): calcd. C 64.16, H 5.92; found C 63.84, H 6.06.

4-Methoxybenzyl 2,3-Di-*O*-benzoyl-α-L-arabinopyranoside (15): Benzoyl chloride (1.1 mL, 9.6 mmol, 1.1 equiv.) was added to a solution of compound **18** (3.2 g, 8.7 mmol) in pyridine (70 mL) at −35 °C. After stirring for 4 h at this temperature, the reaction was quenched by the addition of MeOH. The mixture was taken up in EtOAc (400 mL) and washed with 3 N H_2SO_4 (300 mL), satd. $NaHCO_3$ (300 mL), and H_2O (300 mL). The dried solution (Na_2SO_4) was then evaporated under reduced pressure to give a crude solid, which was purified by column chromatography (cyclohexane/EtOAc, 6:1 to 1.5:1) to give the 2,3 di-*O*-benzoylated compound **15** (3.1 g, 74%), as well as recovered starting material **18** (0.619 g, 19%). Two other compounds were identified: the 2,4 di-*O*-benzoylated compound **19** (0.157 g, 4%) and the 2,3,4 tri-*O*-benzoylated compound **16** (0.131 g, 3%).

Compound 15: R_f = 0.30 (cyclohexane/EtOAc, 6:4). $[\alpha]_D$ = +47.3 (c = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 3.76 (dd, $J_{5a,5b}$ = 12.2, $J_{4,5a}$ = 2.5 Hz, 1 H, H-5a), 3.81 (s, 3 H, OCH_3), 4.16 (dd, $J_{5a,5b}$ = 12.2, $J_{4,5b}$ = 5.2 Hz, 1 H, H-5b), 4.35 (m, 1 H, H-4), 4.60 (d, J = 11.7 Hz, 1 H, CH_2MPM), 4.75 (d, $J_{1,2}$ = 5.5 Hz, 1 H, H-1), 4.84 (d, J = 11.7 Hz, 1 H, CH_2MPM), 5.37 (dd, $J_{2,3}$ = 7.7, $J_{3,4}$ = 3.2 Hz, 1 H, H-3), 5.64 (dd, $J_{2,3}$ = 7.7, $J_{1,2}$ = 5.5 Hz, 1 H, H-2), 6.79 (dd, J = 6.8, 1.8 Hz, 2 H, Ar-H), 7.22 (d, J = 8.6 Hz, 2 H, Ar-H), 7.36 (t, J = 7.9 Hz, 2 H, Ar-H), 7.44 (t, J = 7.9 Hz, 2 H, Ar-H), 7.54 (t, J = 7.5 Hz, 1 H, Ar-H), 7.58 (t, J = 7.5 Hz, 1 H, Ar-H), 7.99 (m, 4 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.2 (OCH$_3$), 63.6 (C-5), 66.2 (C-4), 69.7 (C-2), 69.7 (CH$_2$MPM), 72.5 (C-3), 98.2 (C-1), 113.7 (CH), 128.3 (CH), 128.4 (CH), 128.9 (C), 129.1 (C), 129.3 (C), 129.6 (CH), 129.8 (CH), 129.9 (CH), 133.2 (CH), 133.3 (CH), 159.3 (C), 165.1 (CO), 166.0 (CO) ppm. ESI-MS: m/z = 497 [M + H_2O + H]$^+$. $C_{27}H_{26}O_8$ (478.50): calcd. C 67.77, H 5.48; found C 67.75, H 5.71.

Compound 16: R_f = 0.51 (cyclohexane/EtOAc, 6:4). $[\alpha]_D$ = +115.8 (c = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 3.81 (s, 3 H, OCH_3), 3.90 (dd, $J_{5a,5b}$ = 12.6, $J_{4,5a}$ = 2.0 Hz, 1 H, H-5a), 4.37 (dd, $J_{5a,5b}$ = 12.6, $J_{4,5b}$ = 4.5 Hz, 1 H, H-5b), 4.64 (d, J = 11.8 Hz, 1 H, CH_2MPM), 4.81 (d, $J_{1,2}$ = 6.0 Hz, 1 H, H-1), 4.88 (d, J = 11.8 Hz, 1 H, CH_2MPM), 5.59 (dd, $J_{2,3}$ = 8.3, $J_{3,4}$ = 3.3 Hz, 1 H, H-3), 5.70 (m, 1 H, H-4), 5.76 (dd, $J_{2,3}$ = 8.2, $J_{1,2}$ = 6.2 Hz, 1 H, H-2), 6.79 (d, J = 8.5 Hz, 2 H, Ar-H), 7.22 (d, J = 8.5 Hz, 2 H, Ar-H), 7.30 (m, 2 H, Ar-H), 7.45 (m, 5 H, Ar-H), 7.59 (m, 2 H, Ar-H), 7.90 (d, J = 7.2 Hz, 2 H, Ar-H), 8.00 (d, J = 7.2 Hz, 2 H, Ar-H), 8.06 (d, J = 7.2 Hz, 2 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.2 (OCH$_3$), 62.1 (C-5), 68.2 (C-4), 69.9 (C-2), 70.0 (CH$_2$MPM), 70.2 (C-3), 99.6 (C-1), 113.7 (CH), 128.3 (CH), 128.3 (CH), 128.4 (CH), 128.8 (C), 129.0 (C), 129.3 (C), 129.7 (CH), 129.8 (CH), 133.2 (CH), 133.3 (CH), 165.1 (CO), 165.5 (CO), 165.7 (CO) ppm. ESI-MS: m/z = 601 [M + H_2O + H]$^+$.

4-Methoxybenzyl 2,4-Di-*O*-benzoyl-α-L-arabinopyranoside (19): Trimethyl orthobenzoate (3.0 mL, 17.1 mmol, 2.0 equiv.) and *p*-toluenesulfonic acid (0.325 g, 1.7 mmol, 0.2 equiv.) were added to a stirred solution of compound **18** (3.2 g, 8.5 mmol) in CH_2Cl_2 (70 mL). After 2 h, the solvent was evaporated under reduced pressure and 80% AcOH (25 mL) was added. The reaction mixture was stirred for 10 min then diluted in CH_2Cl_2 (500 mL). The organic layer was washed with H_2O (400 mL), satd. $NaHCO_3$ (2 × 400 mL), and satd. NaCl (400 mL). The dried solution (Na_2SO_4) was then evaporated under reduced pressure to give a crude residue (6.4 g), which was purified by column chromatography (cyclohexane/EtOAc, 6:1 to 2.3:1) to give the desired 2,4 di-*O*-benzoylated compound **19** (3.0 g, 72%) as well as the 2,3 di-*O*-benzoylated compound **15** (1.1 g, 26%). **19:** R_f = 0.41 (cyclohexane/EtOAc, 6:4). $[\alpha]_D$ = +25.2 (c = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 3.82 (s, 3 H, OCH_3), 3.83 (dd, $J_{5a,5b}$ = 12.3, $J_{4,5a}$ = 2.6 Hz, 1 H, H-5a), 4.19 (dd, $J_{2,3}$ = 6.9, $J_{3,4}$ = 3.3 Hz, 1 H, H-3), 4.24 (dd, $J_{5a,5b}$ = 12.3, $J_{4,5b}$ = 6.4 Hz, 1 H, H-5b), 4.62 (d, J = 11.8 Hz, 1 H, CH_2MPM), 4.82 (d, $J_{1,2}$ = 5.0 Hz, 1 H, H-1), 4.83 (d, J = 12.2 Hz, 1 H, CH_2MPM), 5.40 (dd, $J_{2,3}$ = 6.9, $J_{1,2}$ = 4.8 Hz, 1 H, H-2), 5.46 (m, 1 H, H-4), 6.86 (d, J = 8.6 Hz, 2 H, Ar-H), 7.27 (d, J = 8.6 Hz, 2 H, Ar-H), 7.48 (m, 4 H, Ar-H), 7.62 (m, 2 H, Ar-H), 8.06 (d, J = 8.4 Hz, 2 H, Ar-H), 8.13 (d, J = 8.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.2 (OCH$_3$), 60.0 (C-5), 69.3 (C-3), 69.5 (C-4), 69.9 (CH$_2$MPM), 72.1 (C-2), 97.6 (C-1), 113.9 (CH), 128.4 (CH), 129.2 (C), 129.4 (C), 129.8 (CH), 129.9 (CH), 133.4 (CH), 133.5 (CH), 159.5 (C), 165.9 (CO), 166.0 (CO) ppm. ESI-MS: m/z = 501 [M + Na]$^+$. $C_{27}H_{26}O_8$ (478.50): calcd. C 67.77, H 5.48; found C 67.56, H 5.57.

4-Methoxybenzyl (2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzoyl-α-L-arabinopyranoside (21): Alcohol **14** (1.0 g, 2.1 mmol), trichloroacetimidate **20**[23] (1.9 g, 3.1 mmol, 1.5 equiv.), and 4-Å powdered molecular sieves (3 g) were stirred for 1 h at room temperature in CH_2Cl_2 (51 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 (1.05 mL, 0.1 mmol, 0.05 equiv.). After stirring for 2 h at this temperature, the reaction mixture was quenched with triethylamine and filtered through Celite, and then the solvents were evaporated. The crude residue was purified by column chromatography (toluene/EtOAc, 99:1 to 32:1) to give disaccharide **21** (1.9 g, 95%) as an amorphous solid. R_f = 0.35 (toluene/EtOAc, 9:1). $[\alpha]_D$ = +139.0 (c = 1, $CHCl_3$). ^{1}H NMR

($CDCl_3$): δ = 1.08 (d, $J_{5',6'}$ = 6.2 Hz, 3 H, H-6′), 3.61 (s, 3 H, OCH_3), 3.94 (dd, $J_{5a,5b}$ = 13.1, $J_{4,5a}$ = 1.0 Hz, 1 H, H-5a), 4.34 (dd, $J_{5a,5b}$ = 13.1, $J_{4,5b}$ = 2.6 Hz, 1 H, H-5b), 4.37 (dd, $J_{2,3}$ = 9.4, $J_{1,2}$ = 7.1 Hz, 1 H, H-2), 4.56 (m, 1 H, H-5′), 4.66 (d, J = 10.9 Hz, 1 H, CH_2MPM), 4.79 (d, $J_{1,2}$ = 7.0 Hz, 1 H, H-1), 5.01 (d, J = 10.9 Hz, 1 H, CH_2MPM), 5.31 (d, $J_{1',2'}$ = 1.2 Hz, 1 H, H-1′), 5.51 (dd, $J_{2',3'}$ = 3.4, $J_{1',2'}$ = 1.5 Hz, 1 H, H-2′), 5.55 (dd, $J_{2,3}$ = 9.4, $J_{3,4}$ = 3.5 Hz, 1 H, H-3), 5.58 (t, $J_{3',4'}$ = $J_{4',5'}$ = 10.1 Hz, 1 H, H-4′), 5.69 (m, 1 H, H-4), 5.83 (dd, $J_{3',4'}$ = 10.1, $J_{2',3'}$ = 3.5 Hz, 1 H, H-3′), 6.80 (d, J = 8.6 Hz, 2 H, Ar-H), 7.25 (m, 4 H, Ar-H), 7.44 (m, 10 H, Ar-H), 7.59 (m, 3 H, Ar-H), 7.78 (d, J = 7.7 Hz, 2 H, Ar-H), 7.82 (d, J = 7.6 Hz, 2 H, Ar-H), 7.91 (d, J = 7.2 Hz, 2 H, Ar-H), 7.98 (d, J = 7.6 Hz, 2 H, Ar-H), 8.06 (d, J = 7.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.0 (C-6′), 55.0 (OCH_3), 63.8 (C-5), 67.1 (C-5′), 69.2 (C-4), 69.5 (C-3′), 70.4 (C-2′), 71.0 (CH_2MPM), 71.7 (C-4′), 73.6 (C-3), 74.2 (C-2), 98.3 (C-1′), 100.5 (C-1), 113.8 (CH), 128.1 (CH), 128.3 (CH), 128.5 (CH), 128.6 (C), 129.0 (C), 129.0 (C), 129.3 (C), 129.4 (C), 129.6 (CH), 129.7 (CH), 129.8 (CH), 130.3 (CH), 133.0 (CH), 133.1 (CH), 133.3 (CH), 159.5 (C), 164.7 (CO), 165.4 (CO), 165.5 (CO), 165.7 (CO), 165.7 (CO) ppm. ESI-MS: m/z = 959 [M + Na]$^+$. $C_{54}H_{48}O_{15}$ (936.97): calcd. C 69.22, H 5.16; found C 69.17, H 5.54.

4-Methoxybenzyl (2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→3)-2,4-di-*O*-benzoyl-α-L-arabinopyranoside (22): This compound was prepared from alcohol **19** (0.5 g, 1 mmol), trichloroacetimidate **20** (0.954 g, 1.6 mmol, 1.5 equiv.), and a 0.1 M solution of TMSOTf in CH_2Cl_2 (0.520 mL, 0.05 mmol, 0.05 equiv.) in the same manner as that described for **21**. The product was purified by column chromatography (toluene/EtOAc, 199:1 to 19:1) to give the disaccharide **22** (0.950 g, 97%) as an amorphous solid. R_f = 0.38 (toluene/EtOAc, 9:1). $[\alpha]_D$ = +103.2 (c = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 1.10 (d, $J_{5',6'}$ = 6.3 Hz, 3 H, H-6′), 3.71 (s, 3 H, OCH_3), 3.82 (dd, $J_{5a,5b}$ = 15.3, $J_{4,5a}$ = 3.2 Hz, 1 H, H-5a), 4.20 (m, 1 H, H-5′), 4.37 (dd, $J_{2,3}$ = 6.7, $J_{3,4}$ = 3.3 Hz, 1 H, H-3), 4.47 (dd, $J_{5a,5b}$ = 12.2, $J_{4,5b}$ = 6.2 Hz, 1 H, H-5b), 4.63 (d, J = 12.0 Hz, 1 H, CH_2MPM), 4.80 (d, $J_{1,2}$ = 4.8 Hz, 1 H, H-1), 4.89 (d, J = 12.0 Hz, 1 H, CH_2MPM), 5.32 (d, $J_{1',2'}$ = 1.4 Hz, 1 H, H-1′), 5.54 (m, 1 H, H-2′), 5.56 (t, $J_{3',4'}$ = $J_{4',5'}$ = 10.0 Hz, 1 H, H-4′), 5.60 (dt, $J_{4,5a}$ = 6.2, $J_{3,4}$ = $J_{4,5e}$ = 3.1 Hz, 1 H, H-4), 5.65 (dd, $J_{2,3}$ = 6.6, $J_{1,2}$ = 5.2 Hz, 1 H, H-2), 5.78 (dd, $J_{3',4'}$ = 10.1, $J_{2',3'}$ = 3.4 Hz, 1 H, H-3′), 6.80 (d, J = 8.4 Hz, 2 H, Ar-H), 7.15−7.64 (m, 17 H, Ar-H), 7.80 (m, 4 H, Ar-H), 8.02 (m, 2 H, Ar-H), 8.10 (m, 2 H, Ar-H), 8.24 (m, 2 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.2 (C-6′), 55.1 (OCH_3), 60.7 (C-5), 67.3 (C-5′), 69.0 (C-4), 69.4 (C-3′), 69.7 (CH_2MPM), 69.9 (C-2), 70.6 (C-2′), 71.5 (C-4′), 74.4 (C-3), 97.4 (C-1′), 97.9 (C-1), 113.8 (CH), 128.1 (CH), 128.3 (CH), 128.4 (CH), 128.6 (CH), 129.0 (C), 129.1 (C), 129.2 (C), 129.3 (C), 129.4 (C), 129.5 (CH), 129.6 (CH), 129.7 (CH), 129.8 (CH), 129.9 (CH), 132.9 (CH), 133.2 (CH), 133.3 (CH), 133.4 (CH), 159.2 (C), 164.9 (CO), 165.1 (CO), 165.2 (CO), 165.5 (CO), 166.0 (CO) ppm. ESI-MS: m/z = 959 [M + Na]$^+$. $C_{54}H_{48}O_{15}$ (936.97): calcd. C 69.22, H 5.16; found C 68.83, H 5.08.

4-Methoxybenzyl (2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→4)-2,3-di-*O*-benzoyl-α-L-arabinopyranoside (23): This compound was prepared from alcohol **15** (0.5 g, 1 mmol), trichloroacetimidate **20** (0.763 g, 1.3 mmol, 1.2 equiv.), and a 0.1 M solution of TMSOTf in CH_2Cl_2 (0.520 mL, 0.05 mmol, 0.05 equiv.) in the same manner as that described for **21**. The product was purified by column chromatography (toluene/EtOAc, 99:1 to 19:1) to give the disaccharide **23** (0.960 g, 98%) as an amorphous solid. R_f = 0.37 (toluene/EtOAc, 9:1). $[\alpha]_D$ = +90.3 (c = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 1.41 (d, $J_{5',6'}$ = 6.2 Hz, 3 H, H-6′), 3.82 (dd, $J_{5a,5b}$ = 11.8, $J_{4,5a}$ = 2.8 Hz, 1 H, H-5a), 3.84 (s, 3 H, OCH_3), 4.35 (m, 1 H, H-5′), 4.38 (dd, $J_{5a,5b}$ = 11.8, $J_{4,5b}$ = 6.5 Hz, 1 H, H-5b), 4.44 (m, 1 H, H-4), 4.63 (d, J = 11.4 Hz, 1 H, CH_2MPM), 4.89 (m, 1 H, H-1), 4.90 (d, J = 11.6 Hz, 1 H, CH_2MPM), 5.28 (s, 1 H, H-1′), 5.64 (m, 2 H, H-2, H-3), 5.68 (t, $J_{3',4'}$ = $J_{4',5'}$ = 10.0 Hz, 1 H, H-4′), 5.70 (m, 1 H, H-2′), 5.84 (dd, $J_{3',4'}$ = 10.1, $J_{2',3'}$ = 3.3 Hz, 1 H, H-3′), 6.86 (dd, J = 6.8, J = 1.8 Hz, 2 H, Ar-H), 7.24−7.63 (m, 17 H, Ar-H), 7.82 (m, 2 H, Ar-H), 7.98−8.09 (m, 8 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.6 (C-6′), 55.2 (OCH_3), 61.3 (C-5), 67.4 (C-5′), 69.0 (C-3), 69.6 (C-3′), 69.9 (CH_2MPM), 70.0 (C-2), 70.4 (C-2′), 71.6 (C-4), 71.7 (C-4′), 97.5 (C-1′), 97.9 (C-1), 113.8 (CH), 128.1 (CH), 128.3 (CH), 128.5 (CH), 129.1 (C), 129.2 (C), 129.3 (C), 129.4 (C), 129.6 (CH), 129.8 (CH), 129.9 (CH), 130.0 (CH), 132.0 (CH), 133.1 (CH), 133.3 (CH), 159.3 (C), 164.9 (CO), 165.0 (CO), 165.1 (CO), 165.7 (CO), 165.8 (CO) ppm. ESI-MS: m/z = 959 [M + Na]$^+$. $C_{54}H_{48}O_{15}$ (936.97): calcd. C 69.22, H 5.16; found C 68.98, H 5.00.

(2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzoyl-β-L-arabinopyranosyl Trichloroacetimidate (24): Trifluoroacetic acid (5.82 mL, 76.1 mmol, 20 equiv.) and H_2O (0.8 mL, 45.7 mmol, 12 equiv.) were added to a solution of the disaccharide **21** (3.57 g, 3.8 mmol) in CH_2Cl_2 (130 mL). The reaction mixture was vigorously stirred overnight before being washed with H_2O, satd. $NaHCO_3$, and satd. NaCl. The dried solution (Na_2SO_4) was then evaporated under reduced pressure and the residue taken up in CH_2Cl_2 (19 mL). Trichloroacetonitrile (2.7 mL, 26.6 mmol, 7 equiv.) was added, followed by DBU (0.058 mL, 0.38 mmol, 0.1 equiv.), and then the reaction mixture was stirred overnight. The solvent was then evaporated and the crude residue was purified by column chromatography (cyclohexane/EtOAc, 9:1) to give **24** (2.96 g, 81%) as a white amorphous solid. R_f = 0.60 (cyclohexane/EtOAc, 6:4). $[\alpha]_D$ = +169.1 (c = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 1.40 (d, $J_{5',6'}$ = 6.2 Hz, 3 H, H-6′), 4.16 (dd, $J_{5a,5b}$ = 13.3, $J_{4,5a}$ = 1.9 Hz, 1 H, H-5a), 4.26 (m, 1 H, H-5′), 4.40 (br. d, J = 12.8 Hz, 1 H, H-5b), 4.68 (dd, $J_{2,3}$ = 10.5, $J_{1,2}$ = 3.7 Hz, 1 H, H-2), 5.41 (d, $J_{1',2'}$ = 1.5 Hz, 1 H, H-1′), 5.51 (dd, $J_{2',3'}$ = 3.3, $J_{1',2'}$ = 1.7 Hz, 1 H, H-2′), 5.68 (t, $J_{3',4'}$ = $J_{4',5'}$ = 9.9 Hz, 1 H, H-4′), 5.80 (dd, $J_{2,3}$ = 10.5, $J_{3,4}$ = 3.4 Hz, 1 H, H-3), 5.85 (dd, $J_{3',4'}$ = 10.1, $J_{2',3'}$ = 3.4 Hz, 1 H, H-3′), 5.98 (m, 1 H, H-4), 6.73 (d, $J_{1,2}$ = 3.7 Hz, 1 H, H-1), 7.24 (t, J = 7.7 Hz, 2 H, Ar-H), 7.42 (m, 5 H, Ar-H), 7.50 (m, 6 H, Ar-H), 7.63 (m, 2 H, Ar-H), 7.77 (dd, J = 8.1, 1.1 Hz, 2 H, Ar-H), 7.94 (dd, J = 8.0, 1.0 Hz, 2 H, Ar-H), 8.05 (m, 6 H, Ar-H), 8.86 (s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.6 (C-6′), 62.9 (C-5), 67.6 (C-5′), 68.9 (C-3′), 69.5 (C-4), 69.9 (C-3), 70.8 (C-2′), 71.6 (C-4′), 74.3 (C-2), 95.7 (C-1), 99.8 (C-1′), 128.2 (CH), 128.4 (CH), 128.5 (CH), 128.6 (CH), 129.1 (C), 129.4 (C), 129.6 (C), 129.7 (CH), 129.8 (CH), 129.9 (CH), 133.0 (CH), 133.2 (CH), 133.4 (CH), 133.5 (CH), 161.6 (C=NH), 165.0 (CO), 165.1 (CO), 165.5 (CO), 165.6 (CO), 165.8 (CO) ppm. ESI-MS: m/z = 1007 [M + 2Na]$^+$. $C_{48}H_{40}Cl_3NO_{14}$ (961.20): calcd. C 59.98, H 4.19, N 1.46; found C 60.36, H 4.40, N 1.41.

(2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→3)-2,4-di-*O*-benzoyl-β-L-arabinopyranosyl Trichloroacetimidate (25): This compound was prepared from disaccharide **22** (0.950 g, 1 mmol) in the same manner as that described for compound **24**. Purification by column chromatography (cyclohexane/EtOAc, 9:1 to 6:1) gave **25** (0.769 g, 79%) as an amorphous white solid. R_f = 0.58 (cyclohexane/EtOAc, 3:2). $[\alpha]_D$ = +154.7 (c = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 1.29 (d, $J_{5',6'}$ = 5.9 Hz, 3 H, H-6′), 4.23 (dd, $J_{5a,5b}$ = 13.4, $J_{4,5a}$ = 1.8 Hz, 1 H, H-5a), 4.24 (m, 1 H, H-5′), 4.33 (br. d, J = 12.8 Hz, 1 H, H-5b), 4.69 (dd, $J_{2,3}$ = 10.3, $J_{3,4}$ = 3.5 Hz, 1 H, H-3), 5.41 (d, $J_{1',2'}$ = 1.5 Hz, 1 H, H-1′), 5.50 (dd, $J_{2',3'}$ = 3.1,

$J_{1',2'}$ = 1.7 Hz, 1 H, H-2′), 5.59 (t, $J_{3',4'} = J_{4',5'}$ = 9.9 Hz, 1 H, H-4′), 5.65 (dd, $J_{3',4'}$ = 10.0, $J_{2',3'}$ = 3.2 Hz, 1 H, H-3′), 5.73 (m, 1 H, H-4), 5.84 (dd, $J_{2,3}$ = 10.3, $J_{1,2}$ = 3.5 Hz, 1 H, H-2), 6.88 (d, $J_{1,2}$ = 3.5 Hz, 1 H, H-1), 7.23−7.77 (m, 19 H, Ar-H), 8.00 (d, J = 8.1 Hz, 2 H, Ar-H), 8.12 (d, J = 8.2 Hz, 2 H, Ar-H), 8.30 (d, J = 8.2 Hz, 2 H, Ar-H), 8.65 (s, 1 H, N*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.5 (C-6′), 63.0 (C-5), 67.6 (C-5′), 69.3 (C-3′), 69.8 (C-2), 70.4 (C-2′), 71.2 (C-4), 71.4 (C-4′), 73.9 (C-3), 94.3 (C-1), 99.6 (C-1′), 128.1 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 128.7 (CH), 128.9 (C), 129.0 (C), 129.1 (C), 129.4 (C), 129.5 (CH), 129.6 (CH), 129.8 (CH), 129.9 (CH), 130.0 (CH), 132.9 (CH), 133.2 (CH), 133.4 (CH), 133.6 (CH), 160.6 (C=NH), 164.8 (CO), 165.1 (CO), 165.5 (CO), 165.8 (CO), 166.3 (CO) ppm. ESI-MS: *m*/*z* = 984 [M + Na]$^+$. $C_{48}H_{40}Cl_3NO_{14}$ (961.20): calcd. C 59.98, H 4.19, N 1.46; found C 60.34, H 4.29, N 1.24.

(2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→4)-2,3-di-*O*-benzoyl-β-L-arabinopyranosyl Trichloroacetimidate (26): This compound was prepared from disaccharide **23** (0.979 g, 1.05 mmol) in the same manner as that described for compound **24**. Purification by column chromatography (cyclohexane/EtOAc, 9:1 to 6:1) gave **26** (0.694 g, 69%) as an amorphous white solid. R_f = 0.60 (cyclohexane/EtOAc, 6:4). $[\alpha]_D$ = +176.1 (c = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 1.40 (d, $J_{5',6'}$ = 6.2 Hz, 3 H, H-6′), 4.22 (dd, $J_{5a,5b}$ = 13.0, $J_{4,5a}$ = 1.8 Hz, 1 H, H-5a), 4. 34 (d, $J_{5a,5b}$ = 12.8 Hz, 1 H, H-5b), 4.48 (m, 1 H, H-5′), 4.52 (m, 1 H, H-4), 5.30 (d, $J_{1',2'}$ = 1.5 Hz, 1 H, H-1′), 5.75 (t, $J_{3',4'} = J_{4',5'}$ = 10.0 Hz, 1 H, H-4′), 5.85 (dd, $J_{2',3'}$ = 3.2, $J_{1',2'}$ = 1.7 Hz, 1 H, H-2′), 5.97 (dd, $J_{2,3}$ = 10.5, $J_{1,2}$ = 3.2 Hz, 1 H, H-2), 5.99 (dd, $J_{3',4'}$ = 9.8, $J_{2',3'}$ = 3.1 Hz, 1 H, H-3′), 6.01 (dd, $J_{3,2}$ = 10.6, $J_{3,4}$ = 3.0 Hz, 1 H, H-3), 6.92 (d, $J_{1,2}$ = 3.2 Hz, 1 H, H-1), 7.29−7.66 (m, 15 H, Ar-H), 7.90 (m, 2 H, Ar-H), 8.03−8.17 (m, 8 H, Ar-H), 8.66 (s, 1 H, N*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.6 (C-6′), 64.1 (C-5), 67.6 (C-5′), 68.3 (C-2), 68.7 (C-3), 69.8 (C-3′), 70.6 (C-2′), 71.5 (C-4′), 76.0 (C-4), 94.3 (C-1), 99.7 (C-1′), 128.3 (CH), 128.4 (CH), 128.5 (CH), 128.6 (CH), 128.9 (C), 129.1 (C), 129.2 (C), 129.7 (CH), 129.8 (CH), 129.9 (CH), 130.0 (CH), 133.0 (CH), 133.4 (CH), 133.5 (CH), 160.9 (C=NH), 165.2 (CO), 165.3 (CO), 165.5 (CO), 165.9 (CO) ppm. ESI-MS: *m*/*z* = 1007 [M + 2Na]$^+$. $C_{48}H_{40}Cl_3NO_{14}$ (961.20): calcd. C 59.98, H 4.19, N 1.46; found C 60.18, H 3.93, N 1.77.

2,3,4-Tri-*O*-benzoyl-L-arabinopyranosyl Trichloroacetimidate (27): Benzoyl chloride (7.5 mL, 64.6 mmol, 6.5 equiv.) was added to a solution of L-arabinose (1.5 g, 10 mmol) in pyridine (23 mL) at 0 °C. The reaction mixture was left to stir at room temp. overnight and was then quenched by addition of MeOH. Toluene was added and the solvent evaporated under reduced pressure (3 ×). The crude residue was taken up in EtOAc (100 mL) and washed with 1 N HCl (30 mL), satd. $NaHCO_3$ (30 mL), and H_2O (30 mL). The dried solution (Na_2SO_4) was then evaporated under reduced pressure to give a crude solid, which was used without purification in the next step. A solution of 33% HBr in AcOH (5 mL) was added to the perbenzoylated arabinose derivative (1.8 g, 3.18 mmol) in CH_2Cl_2 (4.8 mL) at room temp. After stirring overnight, the mixture was diluted with CH_2Cl_2 (150 mL) and then poured into H_2O (100 mL). The organic layer was washed with H_2O (100 mL), satd. $NaHCO_3$ (100 mL), and satd. NaCl (100 mL). The dried solution (Na_2SO_4) was then evaporated under reduced pressure, and the crude residue obtained was taken up in acetone (29 mL) and H_2O (3.7 mL). Sodium iodide was added (0.05 g, 0.3 mmol), and the reaction mixture was stirred for 24 h. The reaction mixture was diluted with EtOAc and the organic layer was washed with H_2O (100 mL), 10% $Na_2S_2O_3$ (100 mL), satd. $NaHCO_3$ (100 mL), and H_2O (100 mL). The dried solution (Na_2SO_4) was then evaporated to give a crude residue (2 g), which was dissolved in CH_2Cl_2 (40 mL). Trichloroacetonitrile (1.6 mL, 16.0 mmol, 5 equiv.) and DBU (4 drops) were added. After 4 h, the solvent was evaporated, and the crude residue purified by column chromatography (cyclohexane/EtOAc, 19:1 to 6:1) to give the β-trichloroacetimidate (0.5 g, 24%), and the α anomer (1.1 g, 53%). Leaving the reaction overnight gave exclusively the thermodynamically more stable β-trichloroacetimidate.

2,3,4-Tri-*O*-benzoyl-β-L-arabinopyranosyl Trichloroacetimidate-$^4C_1$: R_f = 0.65 (cyclohexane/EtOAc, 6:4). $[\alpha]_D$ = +183.0 (c = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 4.22 (dd, $J_{5a,5b}$ = 13.3, $J_{5a,4}$ = 1.9 Hz, 1 H, H-5a), 4.46 (br. d, $J_{5a,5b}$ = 13.3 Hz, 1 H, H-5b), 5.92 (m, 1 H, H-4), 6.04 (dd, $J_{2,3}$ = 10.7, $J_{2,1}$ = 3.2 Hz, 1 H, H-2), 6.07 (dd, $J_{3,2}$ = 10.7, $J_{3,4}$ = 3.1 Hz, 1 H, H-3), 6.86 (d, $J_{1,2}$ = 3.0 Hz, 1 H, H-1), 7.32 (m, 3 H, Ar-H), 7.41 (m, 2 H, Ar-H), 7.54 (m, 3 H, Ar-H), 7.67 (m, 1 H, Ar-H), 7.89 (d, J = 8.1 Hz, 2 H, Ar-H), 8.00 (d, J = 8.1 Hz, 2 H, Ar-H), 8.13 (d, J = 8.0 Hz, 2 H, Ar-H), 8.68 (s, 1 H, N*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 63.1 (C-5), 67.9 (C-2), 67.9 (C-3), 69.4 (C-4), 94.3 (C-1), 128.3 (CH), 128.4 (CH), 128.6 (CH), 128.7 (C), 128.9 (C), 129.3 (C), 129.7 (CH), 129.8 (CH), 129.9 (CH), 133.3 (CH), 133.5 (CH), 133.5 (CH), 160.7 (C=NH), 165.5 (CO), 165.6 (CO) ppm. $C_{28}H_{22}Cl_3NO_8$ (606.84): calcd. C 55.42, H 3.65, N 2.31; found C 55.41, H 3.65, N 2.31.

2,3,4-Tri-*O*-benzoyl-α-L-arabinopyranosyl Trichloroacetimidate-$^1C_4$: R_f = 0.59 (cyclohexane/EtOAc, 6:4). $[\alpha]_D$ = +74.1 (c = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 4.14 (dd, $J_{5a,5b}$ = 11.9, $J_{4,5a}$ = 3.7 Hz, 1 H, H-5a) 4.50 (dd, $J_{5a,5b}$ = 12.0, $J_{4,5b}$ = 7.6 Hz, 1 H, H-5b), 5.80 (m, 1 H, H-4), 5.84 (m, 2 H, H-2, H-3), 6.36 (s, 1 H, H-1), 7.47 (m, 6 H, Ar-H), 7.59 (m, 3 H, Ar-H), 8.00 (m, 2 H, Ar-H), 8.13 (m, 4 H, Ar-H), 8.82 (s, 1 H, N*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 60.8 (C-5), 66.5 (C-4), 68.5 (C-3), 68.9 (C-2), 94.7 (C-1), 128.4 (CH), 128.4 (CH), 128.5 (CH), 128.7 (C), 129.0 (C), 129.1 (C), 129.9 (CH), 130.1 (CH), 133.5 (CH), 133.7 (CH), 160.8 (C=NH), 164.8 (CO), 165.4 (CO).

Methyl 23-*O*-Benzoylhederagenate (29): Benzoyl chloride (0.79 mL, 6.8 mmol, 1.4 equiv.) was slowly added to a mixture of methyl hederagenate **28** (2.38 g, 4.9 mmol) in pyridine (50 mL, 618 mmol, 127 equiv.) and CH_2Cl_2 (80 mL) at room temperature. After stirring for 1 h the reaction mixture was quenched by the addition of methanol. Further CH_2Cl_2 (120 mL) was added and the organic layer was washed with 1 N HCl (150 mL), satd. $NaHCO_3$ (150 mL), and satd. NaCl (150 mL). The dried solution (Na_2SO_4) was then evaporated under reduced pressure and the crude residue purified by column chromatography (cyclohexane/EtOAc, 99:1 to 7:1) to give **29** (2.1 g, 71%) as a white solid. R_f = 0.58 (cyclohexane/EtOAc, 6:4). M.p. 99 °C. $[\alpha]_D$ = +18.5 (c = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 0.76 (s, 3 H, H-26), 0.87 (s, 3 H, H-24), 0.91 (s, 3 H, H-29), 0.94 (s, 3 H, H-30), 0.99 (s, 3 H, H-25), 1.00−2.05 (m, 22 H), 1.12 (s, 3 H, H-27), 2.88 (dd, J = 13.8, 4.0 Hz, 1 H, H-18), 3.51 (dd, J = 11.2, 5.6 Hz, 1 H, H-3), 3.65 (s, 3 H, OC*H*$_3$) 4.02 (d, J = 11.5 Hz, 1 H, H-23a), 4.54 (d, J = 11.5 Hz, 1 H, H-23b), 5.31 (m, 1 H, H-12), 7.47 (t, J = 7.9 Hz, 2 H, Ar-H), 7.60 (t, J = 7.4 Hz, 1 H, Ar-H), 8.06 (dd, J = 8.3, 1.2 Hz, 2 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 12.0 (C-24), 15.8 (C-25), 16.8 (C-26), 18.2 (C-6), 23.0 (C-16), 23.3 (C-11), 23.6 (C-30), 25.6 (C-27), 26.1 (C-2), 27.6 (C-15), 30.6 (C-20), 32.3 (C-22), 32.4 (C-7), 33.1 (C-29), 33.8 (C-21), 36.8 (C-10), 38.4 (C-1), 39.2 (C-8), 41.3 (C-18), 41.5 (C-14), 42.5 (C-4), 45.8 (C-19), 46.7 (C-17), 48.0 (C-9), 48.2 (C-5), 51.5 (O*C*H$_3$), 66.7 (C-23), 72.3 (C-3), 122.2 (C-12), 128.5 (CH), 129.5 (CH), 130.1 (C), 133.1 (CH), 143.7 (C-13), 166.8 (CO), 178.2 (C-28) ppm. $C_{38}H_{54}O_5 \cdot 0.5H_2O$ (599.85): calcd. C 76.09, H 9.24; found C 76.00, H 9.13.

Methyl 3-*O*-[2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-β-L-arabinopyranosyl]-23-*O*-benzoylhederagenate (30): Acceptor **29** (0.070 g, 0.12 mmol), trichloroacetimidate **24** (0.17 g, 0.18 mmol, 1.5 equiv.), and powdered 4 Å molecular sieves (0.650 g) were stirred for 1 h at room temperature in CH_2Cl_2 (3 mL). The mixture was cooled to −20 °C for 30 min followed by the dropwise addition of a 0.1 M solution of TMSOTf in CH_2Cl_2 (0.060 mL, 0.006 mmol, 0.05 equiv.). After 1 h the reaction mixture was quenched with triethylamine, filtered through Celite, and the solvents were evaporated. Purification by column chromatography (toluene/EtOAc, 99:1 to 32:1) gave a mixture of α and β anomers, which were then separated by HPLC (100% acetonitrile) to give the β anomer **30** (0.134 g, 81%) and the α anomer **31** (0.013 g, 8%).

Compound 30 (β anomer): R_f = 0.46 (toluene/EtOAc, 9:1). $[\alpha]_D$ = +151.3 (c = 1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 0.81 (s, 3 H, H-26), 0.93 (s, 3 H, H-29), 0.96 (s, 3 H, H-30), 1.00−2.10 (m, 22 H), 1.08 (s, 3 H, H-27), 1.10 (s, 3 H, H-25), 1.17 (s, 3 H, H-24), 1.38 (d, $J_{5'',6''}$ = 6.2 Hz, 3 H, H-6″), 2.91 (dd, J = 13.7, 3.8 Hz, 1 H, H-18), 3.68 (s, 3 H, OCH_3), 3.87 (d, $J_{5'a,5'b}$ = 11.7 Hz, 1 H, H-5′a), 3.97 (dd, J = 11.2, 3.8 Hz, 1 H, H-3), 4.21 (d, $J_{5'a,5'b}$ = 11.8 Hz, 1 H, H-5′b), 4.36 (m, 1 H, H-5″), 4.48 (s, 2 H, H-23), 4.53 (dd, $J_{2',3'}$ = 10.4, $J_{1',2'}$ = 3.6 Hz, 1 H, H-2′), 5.34 (m, 1 H, H-12), 5.39 (s, 1 H, H-1″), 5.41 (d, $J_{1',2'}$ = 3.7 Hz, 1 H, H-1′), 5.53 (dd, $J_{2'',3''}$ = 3.1, $J_{1'',2''}$ = 1.9 Hz, 1 H, H-2″), 5.67 (t, $J_{3'',4''} = J_{4'',5''}$ = 9.9 Hz, 1 H, H-4″), 5.74 (dd, $J_{2',3'}$ = 10.4, $J_{3',4'}$ = 3.3 Hz, 1 H, H-3′), 5.83 (m, 1 H, H-4′), 5.90 (dd, $J_{3'',4''}$ = 10.0, $J_{2'',3''}$ = 3.3 Hz, 1 H, H-3″), 7.20−8.10 (m, 30 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.2 (C-24), 15.7 (C-25), 16.9 (C-26), 17.7 (C-6″), 18.1 (C-6), 21.4 (C-2), 23.0 (C-16), 23.5 (C-11), 23.6 (C-30), 25.4 (C-27), 27.6 (C-15), 30.7 (C-20), 32.3 (C-22), 32.4 (C-7), 33.1 (C-29), 33.8 (C-21), 36.8 (C-10), 38.1 (C-1), 39.3 (C-8), 41.4 (C-18), 41.6 (C-14), 42.3 (C-4), 45.8 (C-19), 46.7 (C-17), 48.1 (C-9), 48.3 (C-5), 51.5 (OCH_3), 60.9 (C-5′), 65.7 (C-23), 67.3 (C-5″), 69.0 (C-3″), 70.2 (C-3′), 70.3 (C-4′), 70.7 (C-2″), 71.9 (C-4″), 73.9 (C-2′), 76.4 (C-3), 94.6 (C-1′), 98.8 (C-1″), 122.1 (C-12), 128.1 (CH), 128.2 (CH), 128.4 (CH), 128.5 (CH), 129.1 (C), 129.2 (C), 129.4 (C), 129.4 (CH), 129.6 (CH), 129.7 (CH), 129.8 (CH), 129.9 (CH), 130.3 (C), 132.9 (CH), 133.0 (CH), 133.2 (CH), 133.4 (CH), 143.9 (C-13), 164.9 (CO), 165.0 (CO), 165.6 (CO), 165.7 (CO), 166.0 (CO), 178.2 (C-28) ppm. ESI-MS: m/z = 1411 $[M + Na]^+$. $C_{84}H_{92}O_{18}$ (1388.63): calcd. C 72.60, H 6.67; found C 72.43, H 6.75.

Compound 31 (α anomer): R_f = 0.58 (toluene/EtOAc, 9:1). $[\alpha]_D$ = +90.6 (c = 1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 0.76 (s, 3 H, H-26), 0.81 (s, 3 H, H-24), 0.90−2.10 (m, 22 H), 0.93 (s, 3 H, H-29), 0.96 (s, 3 H, H-30), 1.00 (s, 3 H, H-25), 1.09 (s, 3 H, H-27), 1.28 (d, $J_{5'',6''}$ = 6.2 Hz, 3 H, H-6″), 2.89 (dd, J = 13.7, 3.7 Hz, 1 H, H-18), 3.65 (s, 3 H, OCH_3), 3.70 (dd, J = 11.6, 4.4 Hz, 1 H, H-3), 3.86 (dd, $J_{5'a,5'b}$ = 11.8, $J_{4',5'a}$ = 2.7 Hz, 1 H, H-5′a), 4.15 (d, J = 11.4 Hz, 1 H, H-23a), 4.30 (dd, $J_{5'a,5'b}$ = 11.8, $J_{4',5'b}$ = 6.3 Hz, 1 H, H-5′b), 4.37 (dd, $J_{2',3'}$ = 6.3, $J_{1',2'}$ = 4.5 Hz, 1 H, H-2′), 4.42 (d, J = 11.7 Hz, 1 H, H-23b), 4.47 (m, 1 H, H-5″), 4.90 (d, $J_{1',2'}$ = 4.1 Hz, 1 H, H-1′), 5.33 (m, 1 H, H-12), 5.41 (s, 1 H, H-1″), 5.59 (dd, $J_{2',3'}$ = 6.6, $J_{3',4'}$ = 3.2 Hz, 1 H, H-3′), 5.64 (t, $J_{4'',5''} = J_{3'',4''}$ = 10.0 Hz, 1 H, H-4″), 5.66 (m, 1 H, H-4′), 5.75 (m, 1 H, H-2″), 5.87 (dd, $J_{3'',4''}$ = 10.2, $J_{2'',3''}$ = 3.3 Hz, 1 H, H-3″), 7.15−7.71 (m, 18 H, Ar-H), 7.90−8.15 (m, 12 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 12.8 (C-24), 15.7 (C-25), 16.8 (C-26), 17.5 (C-6″), 18.0 (C-6), 22.9 (C-16), 23.4 (C-11), 23.6 (C-30), 25.4 (C-27), 25.5 (C-2), 27.5 (C-15), 30.6 (C-20), 32.3 (C-22, C-7), 33.1 (C-29), 33.8 (C-21), 36.5 (C-10), 38.5 (C-1), 39.2 (C-8), 41.3 (C-18), 41.5 (C-14), 42.4 (C-4), 45.7 (C-19), 46.7 (C-17), 48.0 (C-9), 48.1 (C-5), 51.5 (OCH_3), 60.4 (C-5′), 65.4 (C-23), 67.7 (C-4′, C-5″), 69.1 (C-3″), 70.6 (C-2″, C-3′), 71.8 (C-4″), 75.1 (C-2′), 82.2 (C-3), 98.5 (C-1″), 102.4 (C-1′), 122.2 (C-12), 128.0 (CH), 128.2 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 129.1 (C), 129.2 (C), 129.4 (C), 129.4 (CH), 129.5 (C), 129.6 (CH), 129.8 (CH), 129.9 (CH), 130.3 (C), 132.8 (CH), 132.9 (CH), 133.0 (CH), 133.2 (CH), 133.3 (CH), 143.7 (C-13), 164.8 (CO), 165.3 (CO), 165.4 (CO), 165.5 (CO), 165.8 (CO), 165.9 (CO), 178.2 (C-28) ppm. ESI-MS: m/z = 1411 $[M + Na]^+$. $C_{84}H_{92}O_{18}$ (1388.63): calcd. C 72.60, H 6.67; found C 72.51, H 6.96.

Methyl 3-*O*-[2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-arabinopyranosyl]-23-*O*-benzoylhederagenate (31): Acceptor **29** (0.1 g, 0.17 mmol), trichloroacetimidate **24** (0.33 g, 0.34 mmol, 2.0 equiv.), and powdered 4-Å molecular sieves (0.7 g) were stirred for 1 h at room temperature in dry propionitrile (2.4 mL). The mixture was cooled to −78 °C for 30 min followed by the rapid addition of a 0.1 M solution of TMSOTf in propionitrile (0.510 mL, 0.05 mmol, 0.3 equiv.). The reaction mixture was stirred at this temperature until TLC indicated the disappearance of the acceptor. Triethylamine was added and the mixture was filtered through Celite and the solvents evaporated. The crude residue was purified by column chromatography (toluene/EtOAc, 99:1 to 39:1) to give a mixture of anomeric products, which were then separated by HPLC (100% acetonitrile) to give the desired saponoside **31** (0.17 g, 72%), as a white foam, and the β anomer **30** (0.05 g, 21%), which were previously described above.

Methyl 3-*O*-[2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-arabinopyranosyl]-23-*O*-benzoylhederagenate (32): This compound was prepared from acceptor **29** (0.08 g, 0.14 mmol) and trichloroacetimidate **25** (0.20 g, 0.21 mmol, 1.5 equiv.) in the same manner as that described for **30**. Purification by column chromatography (toluene/EtOAc, 99:1 to 32:1) gave the protected saponoside **32** (0.178 g, 94%) as a white foam. R_f = 0.50 (toluene/EtOAc, 9:1). $[\alpha]_D$ = +100.0 (c = 1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 0.73 (s, 3 H, H-26), 0.81 (s, 3 H, H-24), 0.92 (s, 3 H, H-29), 0.94 (s, 3 H, H-30), 1.00−2.10 (m, 22 H), 1.02 (s, 3 H, H-25), 1.04 (s, 3 H, H-27), 1.08 (d, $J_{5'',6''}$ = 6.2 Hz, 3 H, H-6″), 2.87 (dd, J = 13.8, 3.9 Hz, 1 H, H-18), 3.64 (s, 3 H, OCH_3), 3.66 (dd, J = 11.5, 4.9 Hz, 1 H, H-3), 3.77 (dd, $J_{5'a,5'b}$ = 12.3, $J_{4',5'a}$ = 2.3 Hz, 1 H, H-5′a), 4.06 (d, J = 11.6 Hz, 1 H, H-23a), 4.19 (d, J = 11.6 Hz, 1 H, H-23b), 4.21 (m, 1 H, H-5″), 4.37 (m, 1 H, H-3′), 4.45 (dd, $J_{5'a,5'b}$ = 12.2, $J_{4',5'b}$ = 5.2 Hz, 1 H, H-5′b), 4.82 (d, $J_{1',2'}$ = 4.8 Hz, 1 H, H-1′), 5.31 (m, 2 H, H-1″, H-12), 5.55 (m, 3 H, H-2″, H-4″, H-4′), 5.65 (t, $J_{1',2'} = J_{2',3'}$ = 4.2 Hz, 1 H, H-2′), 5.75 (dd, $J_{3'',4''}$ = 10.0, $J_{2'',3''}$ = 2.7 Hz, 1 H, H-3″), 7.26−8.24 (m, 30 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 12.8 (C-24), 15.4 (C-25), 16.8 (C-26), 17.2 (C-6″), 18.0 (C-6), 22.9 (C-16), 23.4 (C-11), 23.6 (C-30), 25.3 (C-2), 25.4 (C-27), 27.5 (C-15), 30.6 (C-20), 32.3 (C-7, C-22), 33.1 (C-29), 33.8 (C-21), 36.5 (C-10), 38.4 (C-1), 39.2 (C-8), 41.3 (C-18), 41.5 (C-14), 42.2 (C-4), 45.8 (C-19), 46.7 (C-17), 48.0 (C-9), 48.1 (C-5), 51.5 (OCH_3), 61.2 (C-5′), 65.5 (C-23), 67.3 (C-5″), 69.6 (C-3″, C-2″), 70.5 (C-2′, C-4′), 71.4 (C-4″), 75.2 (C-3′), 82.4 (C-3), 98.0 (C-1″), 102.2 (C-1′), 122.3 (C-12), 128.2 (CH), 128.3 (CH), 128.4 (CH), 128.6 (CH), 129.1 (C), 129.2 (C), 129.3 (C), 129.4 (CH), 129.5 (C), 129.6 (CH), 129.8 (CH), 129.9 (CH), 130.0 (CH), 130.4 (C), 132.8 (CH), 132.9 (CH), 133.2 (CH), 133.3 (CH), 133.4 (CH), 143.7 (C-13), 165.0 (CO), 165.2 (CO), 165.5 (CO), 165.8 (CO), 166.1 (CO), 178.2 (C-28) ppm. ESI-MS: m/z = 1411 $[M + Na]^+$. $C_{84}H_{92}O_{18}$ (1388.63): calcd. C 72.60, H 6.67; found C 72.53, H 6.70.

Methyl 3-*O*-[2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-benzoyl-α-L-arabinopyranosyl]-23-*O*-benzoylhederagenate (33): This compound was prepared from acceptor **29** (0.080 g,

0.14 mmol) and trichloroacetimidate **26** (0.20 g, 0.21 mmol, 1.5 equiv.) in the same manner as that described for **30**. Purification by column chromatography (toluene/EtOAc, 99:1 to 32:1) gave the protected saponoside **33** (0.170 g, 90%) as a white foam. R_f = 0.50 (toluene/EtOAc, 9:1). $[\alpha]_D$ = +113.1 (c = 1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 0.73 (s, 3 H, H-26), 0.75 (s, 3 H, H-24), 0.83−2.05 (m, 22 H), 0.92 (s, 3 H, H-29), 0.94 (s, 3 H, H-30), 1.00 (s, 3 H, H-25), 1.03 (s, 3 H, H-27), 1.38 (d, $J_{5'',6''}$ = 6.2 Hz, 3 H, H-6″), 2.87 (dd, J = 13.7, 3.9 Hz, 1 H, H-18), 3.64 (s, 3 H, OCH_3), 3.68 (dd, J = 11.3, 4.9 Hz, 1 H, H-3), 3.74 (br. d, $J_{5'a,5'b}$ = 11.2 Hz, 1 H, H-5′a), 4.03 (d, J = 11.5 Hz, 1 H, H-23a), 4.10 (d, J = 11.5 Hz, 1 H, H-23b), 4.32 (dd, $J_{5'a,5'b}$ = 12.5, $J_{4',5'b}$ = 4.5 Hz, 1 H, H-5′b), 4.38 (m, 1 H, H-4′), 4.41 (m, 1 H, H-5″), 4.82 (d, $J_{1',2'}$ = 5.9 Hz, 1 H, H-1′), 5.19 (s, 1 H, H-1″), 5.31 (m, 1 H, H-12), 5.54 (dd, $J_{2',3'}$ = 8.3, $J_{3',4'}$ = 3.2 Hz, 1 H, H-3′), 5.67 (t, $J_{3'',4''}$ = $J_{4'',5''}$ = 10.0 Hz, 1 H, H-4″), 5.74 (m, 2 H, H-2″, H-2′), 5.92 (dd, $J_{3'',4''}$ = 10.1, $J_{2'',3''}$ = 3.4 Hz, 1 H, H-3″), 7.20−8.15 (m, 30 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 12.7 (C-24), 15.6 (C-25), 16.8 (C-26), 17.6 (C-6″), 18.0 (C-6), 22.9 (C-16), 23.4 (C-11), 23.6 (C-30), 25.4 (C-2, C-27), 27.5 (C-15), 30.6 (C-20), 32.3 (C-7, C-22), 33.1 (C-29), 33.8 (C-21), 36.5 (C-10), 38.3 (C-1), 39.2 (C-8), 41.3 (C-18), 41.5 (C-14), 42.2 (C-4), 45.8 (C-19), 46.7 (C-17), 48.0 (C-9), 48.1 (C-5), 51.5 (OCH_3), 63.2 (C-5′), 65.4 (C-23), 67.4 (C-5″), 69.7 (C-3″), 70.4 (C-2′), 70.7 (C-2″), 71.0 (C-3′), 71.7 (C-4″), 73.2 (C-4′), 82.4 (C-3), 98.2 (C-1″), 102.3 (C-1′), 122.2 (C-12), 128.2 (CH), 128.3 (CH), 128.4 (CH), 129.0 (C), 129.2 (C), 129.3 (C), 129.4 (CH), 129.6 (CH), 129.8 (CH), 130.1 (CH), 130.4 (C), 132.8 (CH), 132.9 (CH), 133.1 (CH), 133.3 (CH), 143.7 (C-13), 164.9 (CO), 165.1 (CO), 165.7 (CO), 165.8 (CO), 178.2 (C-28) ppm. ESI-MS: m/z = 1411 $[M + Na]^+$. $C_{84}H_{92}O_{18}$·0.4CH_3OH (1402.46): calcd. C 72.28, H 6.73; found C 72.09, H 6.54.

Methyl 3-*O*-(2,3,4-Tri-*O*-benzoyl-α-L-arabinopyranosyl)-23-*O*-benzoylhederagenate (34): This compound was prepared from acceptor **29** (0.3 g, 0.51 mmol) and trichloroacetimidate **27** (0.46 g, 0.76 mmol, 1.5 equiv.) in the same manner as that described for **30**. The crude residue was purified by column chromatography (toluene/EtOAc, 99:1 to 24:1) to give saponoside **34** (0.391 g, 74%) as a white foam. R_f = 0.55 (toluene/EtOAc, 9:1). $[\alpha]_D$ = +129.7 (c = 1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 0.69 (s, 3 H, H-24), 0.72 (s, 3 H, H-26), 0.91 (s, 3 H, H-29), 0.94 (s, 3 H, H-30), 0.96 (s, 3 H, H-25), 1.00−2.00 (m, 22 H), 1.03 (s, 3 H, H-27), 2.86 (dd, J = 13.6, 3.8 Hz, 1 H, H-18), 3.63 (s, 3 H, OCH_3), 3.67 (dd, J = 11.3, 4.4 Hz, 1 H, H-3), 3.85 (br. d, J = 12.4 Hz, 1 H, H-5′a), 3.94 (d, J = 11.5 Hz, 1 H, H-23a), 4.10 (d, J = 11.5 Hz, 1 H, H-23b), 4.31 (dd, $J_{5'a,5'b}$ = 13.3, $J_{4',5'b}$ = 2.9 Hz, 1 H, H-5′b), 4.81 (d, $J_{1',2'}$ = 7.0 Hz, 1 H, H-1′), 5.30 (m, 1 H, H-12), 5.56 (dd, $J_{2',3'}$ = 9.5, $J_{3',4'}$ = 3.5 Hz, 1 H, H-3′), 5.68 (m, 1 H, H-4′), 5.84 (dd, $J_{2',3'}$ = 9.4, $J_{1',2'}$ = 7.2 Hz, 1 H, H-2′), 7.33 (m, 4 H, Ar-H), 7.48 (m, 6 H, Ar-H), 7.61 (m, 2 H, Ar-H), 7.91 (d, J = 7.4 Hz, 2 H, Ar-H), 8.04 (d, J = 8.6 Hz, 2 H, Ar-H), 8.06 (d, J = 8.9 Hz, 2 H, Ar-H), 8.10 (d, J = 7.4 Hz, 2 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 12.6 (C-24), 15.5 (C-25), 16.8 (C-26), 17.9 (C-6), 22.9 (C-16), 23.4 (C-11), 23.6 (C-30), 25.4 (C-2, C-27), 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), 39.2 (C-8), 41.3 (C-18), 41.5 (C-14), 42.1 (C-4), 45.7 (C-19), 46.6 (C-17), 47.9 (C-9), 48.0 (C-5), 51.5 (OCH_3), 63.3 (C-5′), 65.2 (C-23), 68.8 (C-4′), 70.0 (C-2′), 71.1 (C-3′), 82.8 (C-3), 102.9 (C-1′), 122.2 (C-12), 128.2 (CH), 128.3 (CH), 128.4 (CH), 128.9 (C), 129.0 (C), 129.4 (C), 129.4 (CH), 129.8 (CH), 129.9 (CH), 130.3 (C), 132.9 (CH), 133.2 (CH), 133.3 (CH), 143.7 (C-13), 165.3 (CO), 165.5 (CO), 165.7 (CO), 165.8 (CO), 178.2 (C-28) ppm. ESI-MS: m/z = 1057 $[M + Na]^+$. $C_{64}H_{74}O_{12}$·0.1CH_3OH (1038.49): calcd. C 74.14, H 7.22; found C 73.82, H 7.44.

Methyl 3-*O*-(α-L-Arabinopyranosyl)hederagenate (4): Saponoside **34** (0.291 g, 0.28 mmol) was treated with a solution of 3% KOH in MeOH (29 mL). The reaction mixture was stirred for 48 h before being neutralized with Amberlite IR 120 (H^+ form) and filtered, and then the solvents were evaporated. The crude residue was purified by column chromatography (CH_2Cl_2/MeOH, 39:1) to give the deprotected saponoside **4** (0.162 g, 93%) as an amorphous solid. $[\alpha]_D$ = +42.6 (c = 1, CH_3OH). ^1H NMR (CD_3OD): δ = 0.73 (s, 3 H, H-24), 0.77 (s, 3 H, H-26), 0.80−2.30 (m, 22 H), 0.93 (s, 3 H, H-29), 0.96 (s, 3 H, H-30), 1.00 (s, 3 H, H-25), 1.20 (s, 3 H, H-27), 2.89 (dd, J = 13.8, 4.1 Hz, 1 H, H-18), 3.31 (d, J = 11.8 Hz, 1 H, H-23a), 3.51 (dd, $J_{2',3'}$ = 9.0, $J_{3',4'}$ = 3.3 Hz, 1 H, H-3′), 3.55 (dd, $J_{2',3'}$ = 8.9, $J_{1',2'}$ = 6.8 Hz, 1 H, H-2′), 3.56 (dd, $J_{5'a,5'b}$ = 12.2, $J_{4',5'a}$ = 1.3 Hz, 1 H, H-5′a), 3.62 (d, J = 11.8 Hz, 1 H, H-23b), 3.63 (dd, J = 11.8, 5.5 Hz, 1 H, H-3), 3.64 (s, 3 H, OCH_3), 3.82 (m, 1 H, H-4′), 3.86 (dd, $J_{5'a,5'b}$ = 12.5, $J_{4',5'b}$ = 2.9 Hz, 1 H, H-5′b), 4.33 (d, $J_{1',2'}$ = 6.6 Hz, 1 H, H-1′), 5.27 (m, 1 H, H-12) ppm. ^{13}C NMR (CD_3OD): δ = 12.0 (C-24), 14.9 (C-25), 16.2 (C-26), 17.4 (C-6), 22.5 (C-30), 22.6 (C-16), 23.1 (C-11), 24.9 (C-2), 25.1 (C-27), 27.3 (C-15), 30.1 (C-20), 31.9 (C-7), 32.1 (C-29, 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), 42.4 (C-4), 45.6 (C-19), 46.6 (C-5, C-17), 47.5 (C-9), 50.8 (OCH_3), 63.3 (C-23), 65.4 (C-5′), 68.3 (C-4′), 71.5 (C-2′), 73.0 (C-3′), 81.8 (C-3), 104.9 (C-1′), 122.3 (C-12), 143.6 (C-13), 178.6 (C-28) ppm. ESI-MS: m/z = 620 $[M + 2H]^+$. $C_{36}H_{58}O_8$·1.1H_2O (638.67): calcd. C 67.70, H 9.50; found C 67.67, H 9.56.

Methyl 3-*O*-[α-L-Rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl]-hederagenate (2): This compound was prepared from saponoside **31** (0.475 g, 0.34 mmol) in the same manner as that described for **4**. Purification by column chromatography (CH_2Cl_2/MeOH, 49:1 to 19:1) gave the α-hederin methyl ester **2** (0.196 g, 75%) as an amorphous white solid. $[\alpha]_D$ = +13.7 (c = 1, CH_3OH). ^1H NMR (CD_3OD): δ = 0.72 (s, 3 H, H-24), 0.77 (s, 3 H, H-26), 0.93 (s, 3 H, H-29), 0.96 (s, 3 H, H-30), 1.00 (s, 3 H, H-25), 1.00−2.10 (m, 22 H), 1.20 (s, 3 H, H-27), 1.26 (d, $J_{5'',6''}$ = 6.2 Hz, 3 H, H-6″), 2.89 (dd, J = 13.2, 3.7 Hz, 1 H, H-18), 3.37 (d, J = 11.2 Hz, 1 H, H-23a), 3.40 (t, $J_{3'',4''}$ = $J_{4'',5''}$ = 9.5 Hz, 1 H, H-4″), 3.51 (d, J = 11.2 Hz, 1 H, H-23b), 3.52 (dd, $J_{5'a,5'b}$ = 12.0, $J_{4',5'a}$ = 2.4 Hz, 1 H, H-5′a), 3.64 (m, 1 H, H-3), 3.64 (s, 3 H, OCH_3), 3.73 (m, 2 H, H-2′, H-3′), 3.74 (m, 1 H, H-3″), 3.79 (m, 1 H, H-4′), 3.86 (dd, $J_{5'a,5'b}$ = 12.0, $J_{4',5'b}$ = 4.5 Hz, 1 H, H-5′b), 3.87 (m, 1 H, H-5″), 3.93 (dd, $J_{2'',3''}$ = 3.1, $J_{1'',2''}$ = 1.5 Hz, 1 H, H-2″), 4.57 (d, $J_{1',2'}$ = 5.2 Hz, 1 H, H-1′), 5.18 (s, 1 H, H-1″), 5.27 (m, 1 H, H-12) ppm. ^{13}C NMR (CD_3OD): δ = 12.3 (C-24), 14.9 (C-25), 16.2 (C-26), 16.5 (C-6″), 17.3 (C-6), 22.5 (C-30), 22.6 (C-16), 23.0 (C-11), 25.0 (C-27), 25.1 (C-2), 27.3 (C-15), 30.1 (C-20), 31.8 (C-7), 32.0 (C-29), 32.1 (C-22), 33.3 (C-21), 36.1 (C-10), 38.2 (C-1), 39.0 (C-8), 41.3 (C-18), 41.4 (C-14), 42.5 (C-4), 45.6 (C-19), 46.6 (C-5, C-17), 47.5 (C-9), 50.7 (OCH_3), 63.1 (C-23), 63.4 (C-5′), 67.7 (C-4′), 68.7 (C-5″), 70.5 (C-2″), 70.7 (C-3″), 72.2 (C-3′), 72.5 (C-4″), 75.2 (C-2′), 80.7 (C-3), 100.4 (C-1″), 102.9 (C-1′), 122.3 (C-12), 143.6 (C-13), 178.6 (C-28) ppm. ESI-MS: m/z = 766 $[M + 2H]^+$. $C_{42}H_{68}O_{12}$·3.3H_2O (824.45): calcd. C 61.19, H 9.12; found C 61.15, H 8.97.

Methyl 3-*O*-[α-L-Rhamnopyranosyl-(1→2)-β-L-arabinopyranosyl]-hederagenate (6): This compound was prepared from saponoside **30** (0.135 g, 0.10 mmol) in the same manner as that described for **4**. Purification by column chromatography (CH_2Cl_2/MeOH, 49:1 to 19:1) gave the deprotected saponoside **6** (0.067 g, 90%) as an amorphous white solid. $[\alpha]_D$ = +76.4 (c = 1, pyridine). ^1H NMR (CD_3OD): δ = 0.72 (s, 3 H, H-24), 0.77 (s, 3 H, H-26), 0.93 (s, 3 H, H-29), 0.96 (s, 3 H, H-30), 1.01 (s, 3 H, H-25), 1.02−2.1 (m, 22

H), 1.20 (s, 3 H, H-27), 1.27 (d, $J_{5'',6''}$ = 6.3 Hz, 3 H, H-6″), 2.89 (dd, J = 13.6, 3.6 Hz, 1 H, H-18), 3.35 (m, 1 H, H-23a), 3.42 (t, $J_{3'',4''} = J_{4'',5''}$ = 9.5 Hz, 1 H, H-4″), 3.50 (d, J = 11.0 Hz, 1 H, H-23b), 3.59 (dd, $J_{5'a,5'b}$ = 12.4, $J_{4',5'a}$ = 2.2 Hz, 1 H, H-5′a), 3.64 (s, 3 H, OCH_3), 3.67 (dd, $J_{3'',4''}$ = 9.5, $J_{2'',3''}$ = 3.3 Hz, 1 H, H-3″), 3.72 (dd, J = 11.8, 4.2 Hz, 1 H, H-3), 3.78 (m, 1 H, H-5″), 3.85 (dd, $J_{2',3'}$ = 9.5, $J_{1',2'}$ = 3.2 Hz, 1 H, H-2′), 3.90 (m, 1 H, H-4′), 3.93 (dd, $J_{2',3'}$ = 9.5, $J_{3',4'}$ = 3.3 Hz, 1 H, H-3′), 3.95 (m, 1 H, H-5′b), 3.97 (m, 1 H, H-2″), 4.95 (d, $J_{1'',2''}$ = 1.4 Hz, 1 H, H-1″), 5.09 (d, $J_{1',2'}$ = 3.3 Hz, 1 H, H-1′), 5.28 (m, 1 H, H-12) ppm. ^{13}C NMR (CD_3OD): δ = 12.5 (C-24), 14.9 (C-25), 16.2 (C-26), 16.6 (C-6″), 17.3 (C-6), 20.6 (C-2), 22.5 (C-30), 22.6 (C-16), 23.1 (C-11), 25.0 (C-27), 27.3 (C-15), 30.1 (C-20), 31.8 (C-7), 32.0 (C-29), 32.1 (C-22), 33.3 (C-21), 36.4 (C-10), 37.6 (C-1), 39.1 (C-8), 41.3 (C-18), 41.4 (C-14), 42.1 (C-4), 45.6 (C-19), 46.4 (C-5), 46.6 (C-17), 47.4 (C-9), 50.7 (OCH$_3$), 63.2 (C-5′, C-23), 68.6 (C-3′), 68.7 (C-5″), 69.6 (C-4′), 70.6 (C-2″), 71.0 (C-3″), 72.3 (C-4″), 74.0 (C-3), 76.0 (C-2′), 94.2 (C-1′), 102.2 (C-1″), 122.3 (C-12), 143.6 (C-13), 178.6 (C-28) ppm. ESI-MS: m/z = 766 $[M + 2H]^+$. $C_{42}H_{68}O_{12}$·1.4H_2O (790.22): calcd. C 63.84, H 9.03; found C 63.83, H 9.28.

Methyl 3-*O*-[α-L-Rhamnopyranosyl-(1→3)-α-L-arabinopyranosyl]-hederagenate (8): This compound was prepared from saponoside **32** (0.136 g, 0.10 mmol) in the same manner as that described for **4**. Purification by column chromatography (CH_2Cl_2/MeOH, 19:1 to 12:1) gave the deprotected saponoside **8** (0.065 g, 87%) as an amorphous white solid. $[\alpha]_D$ = +22.6 (c = 1, CH_3OH). ^{1}H NMR (CD_3OD): δ = 0.73 (s, 3 H, H-24), 0.77 (s, 3 H, H-26), 0.93 (s, 3 H, H-29), 0.96 (s, 3 H, H-30), 1.00 (s, 3 H, H-25), 1.05−2.10 (m, 22 H), 1.19 (s, 3 H, H-27), 1.27 (d, $J_{5'',6''}$ = 6.2 Hz, 3 H, H-6″), 2.89 (dd, J = 13.7, 3.7 Hz, 1 H, H-18), 3.31 (d, J = 11.3 Hz, 1 H, H-23a), 3.41 (t, $J_{3'',4''} = J_{4'',5''}$ = 9.5 Hz, 1 H, H-4″), 3.58 (d, $J_{5'a,5'b}$ = 12.4 Hz, 1 H, H-5′a), 3.59 (dd, $J_{2',3'}$ = 9.3, $J_{3',4'}$ = 3.3 Hz, 1 H, H-3′), 3.63 (m, 2 H, H-23b, H-3), 3.64 (s, 3 H, OCH_3), 3.68 (dd, $J_{2',3'}$ = 9.2, $J_{1',2'}$ = 7.5 Hz, 1 H, H-2′), 3.81 (dd, $J_{3'',4''}$ = 9.5, $J_{2'',3''}$ = 3.3 Hz, 1 H, H-3″), 3.82 (m, 1 H, H-5″), 3.85 (dd, $J_{5'a,5'b}$ = 12.6, $J_{4',5'b}$ = 2.5 Hz, 1 H, H-5′b), 3.90 (m, 1 H, H-4′), 3.99 (dd, $J_{2'',3''}$ = 3.3, $J_{1'',2''}$ = 1.6 Hz, 1 H, H-2″), 4.35 (d, $J_{1',2'}$ = 7.3 Hz, 1 H, H-1′), 5.05 (d, $J_{1'',2''}$ = 1.3 Hz, 1 H, H-1″), 5.27 (m, 1 H, H-12) ppm. ^{13}C NMR (CD_3OD): δ = 12.0 (C-24), 15.0 (C-25), 16.2 (C-26), 16.5 (C-6″), 17.4 (C-6), 22.6 (C-30, C-16), 23.1 (C-11), 24.9 (C-2), 25.0 (C-27), 27.3 (C-15), 30.1 (C-20), 31.9 (C-7), 32.1 (C-29), 32.2 (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), 42.4 (C-4), 45.6 (C-19), 46.7 (C-17, C-5), 47.5 (C-9), 50.8 (OCH$_3$), 63.3 (C-23), 65.7 (C-5′), 68.4 (C-4′), 68.6 (C-5″), 70.6 (C-2″, C-3″), 70.8 (C-2′), 72.6 (C-4″), 79.6 (C-3′), 81.8 (C-3), 102.2 (C-1″), 105.1 (C-1′), 122.3 (C-12), 143.6 (C-13), 178.6 (C-28) ppm. ESI-MS: m/z = 766 $[M + 2H]^+$. $C_{42}H_{68}O_{12}$·2.1 CH_3OH (832.28): calcd. C 63.64, H 9.25; found C 63.84, H 9.59.

Methyl 3-*O*-[α-L-Rhamnopyranosyl-(1→4)-α-L-arabinopyranosyl]-hederagenate (10): This compound was prepared from saponoside **33** (0.150 g, 0.11 mmol) in the same manner as that described for **4**. Purification by column chromatography (CH_2Cl_2/MeOH, 9:1) gave the deprotected saponoside **10** (0.080 g, 96%) as an amorphous white solid. $[\alpha]_D$ = +27.5 (c = 1, pyridine). ^{1}H NMR (CD_3OD): δ = 0.74 (s, 3 H, H-24), 0.77 (s, 3 H, H-26), 0.93 (s, 3 H, H-29), 0.96 (s, 3 H, H-30), 0.98−2.10 (m, 22 H), 1.00 (s, 3 H, H-25), 1.19 (s, 3 H, H-27), 1.27 (d, $J_{5'',6''}$ = 6.2 Hz, 3 H, H-6″), 2.89 (dd, J = 13.7, 4.0 Hz, 1 H, H-18), 3.31 (d, J = 11.4 Hz, 1 H, H-23a), 3.39 (t, $J_{3'',4''} = J_{4'',5''}$ = 9.5 Hz, 1 H, H-4″), 3.52 (dd, $J_{2',3'}$ = 9.4, $J_{1',2'}$ = 7.2 Hz, 1 H, H-2′), 3.54 (br. d, $J_{5'a,5'b}$ = 11.2 Hz, 1 H, H-5′a), 3.58 (dd, $J_{2',3'}$ = 9.4, $J_{3',4'}$ = 3.4 Hz, 1 H, H-3′), 3.62 (dd, J = 11.7, 4.7 Hz, 1 H, H-3), 3.63 (m, 1 H, H-23b), 3.64 (s, OCH_3), 3.75 (dd, $J_{3'',4''}$ = 9.5, $J_{2'',3''}$ = 3.4 Hz, 1 H, H-3″), 3.81 (m, 1 H, H-5″), 3.85 (m, 1 H, H-4′), 3.98 (m, 1 H, H-5′b), 4.00 (dd, $J_{2'',3''}$ = 3.3, $J_{1'',2''}$ = 1.3 Hz, 1 H, H-2″), 4.31 (d, $J_{1',2'}$ = 7.1 Hz, 1 H, H-1′), 4.96 (d, $J_{1'',2''}$ = 1.3 Hz, 1 H, H-1″), 5.27 (m, 1 H, H-12) ppm. ^{13}C NMR (CD_3OD): δ = 12.0 (C-24), 15.0 (C-25), 16.2 (C-26), 16.5 (C-6″), 17.4 (C-6), 22.5 (C-30), 22.6 (C-16), 23.1 (C-11), 24.9 (C-2), 25.1 (C-27), 27.3 (C-15), 30.1 (C-20), 31.9 (C-7), 32.1 (C-29, 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), 42.4 (C-4), 45.6 (C-19), 46.6 (C-17), 46.7 (C-5), 47.5 (C-9), 50.7 (OCH$_3$), 63.3 (C-23), 64.6 (C-5′), 68.7 (C-5″), 70.7 (C-2″), 70.8 (C-3″), 71.8 (C-2′), 72.6 (C-4″), 72.9 (C-3′), 76.2 (C-4′), 82.1 (C-3), 102.1 (C-1″), 105.1 (C-1′), 122.3 (C-12), 143.6 (C-13), 178.6 (C-28) ppm. ESI-MS: m/z = 766 $[M + 2H]^+$. $C_{42}H_{68}O_{12}$·4.4 CH_3OH (905.98): calcd. C 61.52, H 9.52; found C 61.51, H 9.65.

3-*O*-(α-L-Arabinopyranosyl)hederagenin (δ-Hederin) (3): Lithium iodide (0.89 g, 6.6 mmol, 50 equiv.) was added to a solution of compound **4** (0.082 g, 0.13 mmol) in DMF (8.8 mL) and then the reaction mixture was heated under reflux for 5 days. The solvent was evaporated under reduced pressure and the crude residue passed through a column of hydrophobic resin (Mitsubishi HP20SS), eluting sequentially with H_2O, 20% $Na_2S_2O_3$, H_2O, and CH_3OH. The solvent was evaporated and the residue was purified by column chromatography (CH_2Cl_2/MeOH, 19:1) to give δ-hederin **3** (0.016 g, 20%) as an amorphous white solid. Spectral identification, performed in CD_3OD, was in accordance with published data.[30]

3-*O*-[α-L-Rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl]hederagenin (α-Hederin) (1): This compound was prepared from saponoside **2** (0.196 g, 0.26 mmol) in the same manner as that described for **3**. Final purification by column chromatography (CH_2Cl_2/MeOH, 19:1) gave α-hederin **1** (0.092 g, 48%) as an amorphous white solid that was identical to an authentic sample of α-hederin (TLC). Spectral identification was performed in [D_5]pyridine and was in accordance with published data.[31]

3-*O*-[α-L-Rhamnopyranosyl-(1→2)-β-L-arabinopyranosyl]hederagenin (5): This compound was prepared from saponoside **6** (0.055 g, 0.07 mmol) in the same manner as that described for **3**. Final purification by column chromatography (CH_2Cl_2/MeOH, 19:1) gave saponoside **5** (0.025 g, 46%) as an amorphous white solid. $[\alpha]_D$ = +72.5 (c = 1, pyridine). ^{1}H NMR ([D_5]pyridine): δ = 0.92 (s, 6 H, H-25, H-29), 0.94 (s, 3 H, H-24), 0.95−2.23 (m, 22 H), 0.99 (s, 3 H, H-30), 1.01 (s, 3 H, H-26), 1.24 (s, 3 H, H-27), 1.64 (d, $J_{5'',6''}$ = 6.1 Hz, 3 H, H-6″), 3.28 (dd, J = 13.5, 3.5 Hz, 1 H, H-18), 3.67 (d, J = 10.5 Hz, 1 H, H-23a), 3.97 (d, J = 10.8 Hz, 1 H, H-23b), 4.13 (dd, $J_{5'a,5'b}$ = 11.9, $J_{4',5'a}$ = 1.7 Hz, 1 H, H-5′a), 4.31 (m, 1 H, H-3), 4.33 (t, $J_{3'',4''} = J_{4'',5''}$ = 9.3 Hz, 1 H, H-4″), 4.38 (m, 1 H, H-4′), 4.50 (m, 2 H, H-5″, H-5′b), 4.60 (dd, $J_{3'',4''}$ = 9.3, $J_{2'',3''}$ = 3.2 Hz, 1 H, H-3″), 4.66 (dd, $J_{2',3'}$ = 9.5, $J_{3',4'}$ = 3.2 Hz, 1 H, H-3′), 4.77 (m, 1 H, H-2′), 4.78 (m, 1 H, H-2″), 5.49 (m, 1 H, H-12), 5.73 (d, $J_{1',2'}$ = 3.0 Hz, 1 H, H-1′), 5.86 (s, 1 H, H-1″) ppm. ^{13}C NMR ([D_5]pyridine): δ = 13.7 (C-24), 15.6 (C-25), 17.1 (C-26), 17.8 (C-6), 18.2 (C-6″), 21.3 (C-2), 23.3 (C-16), 23.4 (C-30), 23.6 (C-11), 25.8 (C-27), 27.9 (C-15), 30.6 (C-20), 32.4 (C-7), 32.8 (C-22), 32.9 (C-29), 33.8 (C-21), 36.7 (C-10), 37.9 (C-1), 39.4 (C-8), 41.6 (C-18), 41.8 (C-14), 42.7 (C-4), 46.1 (C-19), 46.3 (C-17), 47.0 (C-5), 47.7 (C-9), 63.8 (C-23), 64.3 (C-5′), 69.4 (C-3′), 69.6 (C-5″), 70.2 (C-4′), 71.8 (C-2″), 72.2 (C-3″), 73.4 (C-4″), 74.7 (C-3), 76.5 (C-2′), 95.4 (C-1′), 103.2 (C-1″), 122.2 (C-12), 144.5 (C-13), 180.1 (C-28) ppm. ESI-MS: m/z = 774 $[M + Na + H]^+$.

$C_{41}H_{66}O_{12}$·1.6H_2O (779.79): calcd. C 63.15, H 8.95; found C 63.02, H 9.17.

3-*O*-[α-L-Rhamnopyranosyl-(1→3)-α-L-arabinopyranosyl]hederagenin (7): This compound was prepared from saponoside **8** (0.068 g, 0.09 mmol) in the same manner as that described for **3**. Final purification by column chromatography (CH_2Cl_2/MeOH, 19:1) gave saponoside **7** (0.021 g, 31%) as an amorphous white solid. $[\alpha]_D$ = +30.6 (*c* = 1, pyridine). ^{1}H NMR ([D$_5$]pyridine): δ = 0.90 (s, 3 H, H-24), 0.92 (s, 3 H, H-25), 0.93 (s, 3 H, H-29), 0.99 (s, 3 H, H-30), 1.01 (s, 3 H, H-26), 1.04−2.23 (m, 22 H), 1.26 (s, 3 H, H-27), 1.67 (d, $J_{5'',6''}$ = 6.2 Hz, 3 H, H-6″), 3.28 (dd, *J* = 13.7, 3.3 Hz, 1 H, H-18), 3.70 (m, 2 H, H-23a, H-5′a), 4.16 (dd, $J_{2',3'}$ = 9.3, $J_{3',4'}$ = 3.0 Hz, 1 H, H-3′), 4.26 (dd, $J_{5'a,5'b}$ = 12.2, $J_{4',5'b}$ = 1.9 Hz, 1 H, H-5′b), 4.27 (m, 1 H, H-3), 4.30 (d, *J* = 11.1 Hz, 1 H, H-23b), 4.34 (t, $J_{3'',4''} = J_{4'',5''}$ = 9.4 Hz, 1 H, H-4″), 4.40 (m, 1 H, H-4′), 4.55 (dd, $J_{2',3'}$ = 9.2, $J_{1',2'}$ = 7.5 Hz, 1 H, H-2′), 4.64 (m, 1 H, H-5″), 4.65 (dd, $J_{3'',4''}$ = 9.2, $J_{2'',3''}$ = 2.9 Hz, 1 H, H-3″), 4.77 (dd, $J_{2'',3''}$ = 3.1, $J_{1'',2''}$ = 1.3 Hz, 1 H, H-2″), 4.99 (d, $J_{1',2'}$ = 7.4 Hz, 1 H, H-1′), 5.48 (m, 1 H, H-12), 6.00 (s, 1 H, H-1″) ppm. ^{13}C NMR ([D$_5$]pyridine): δ = 13.4 (C-24), 15.8 (C-25), 17.2 (C-26), 17.8 (C-6), 18.3 (C-6″), 23.3 (C-16), 23.5 (C-30), 23.6 (C-11), 25.9 (C-27), 25.9 (C-2), 28.0 (C-15), 30.6 (C-20), 32.5 (C-7), 32.9 (C-22), 33.0 (C-29), 33.8 (C-21), 36.6 (C-10), 38.4 (C-1), 39.4 (C-8), 41.6 (C-18), 41.8 (C-14), 43.2 (C-4), 46.1 (C-19), 46.4 (C-17), 47.1 (C-5), 47.8 (C-9), 63.7 (C-23), 66.9 (C-5′), 69.0 (C-4′), 69.7 (C-5″), 71.5 (C-2′), 71.8 (C-2″), 72.1 (C-3″), 73.7 (C-4″), 80.4 (C-3′), 81.7 (C-3), 103.5 (C-1″), 106.5 (C-1′), 122.3 (C-12), 144.5 (C-13), 180.1 (C-28) ppm. ESI-MS: *m*/*z* = 774 [M + Na + H]$^+$. $C_{41}H_{66}O_{12}$·2.7H_2O (799.61): calcd. C 61.59, H 9.00; found C 61.50, H 8.68.

3-*O*-[α-L-Rhamnopyranosyl-(1→4)-α-L-arabinopyranosyl]hederagenin (9): This compound was prepared from saponoside **10** (0.043 g, 0.056 mmol) in the same manner as that described for **3**. Final purification by column chromatography (CH_2Cl_2/MeOH, 12:1) gave saponoside **9** (0.020 g, 47%) as an amorphous white solid. $[\alpha]_D$ = +26.6 (*c* = 1, pyridine). ^{1}H NMR ([D$_5$]pyridine): δ = 0.90 (s, 3 H, H-25), 0.91 (s, 3 H, H-24), 0.92 (s, 3 H, H-29), 0.99 (s, 3 H, H-30), 1.00 (s, 3 H, H-26), 1.01−2.27 (m, 22 H), 1.24 (s, 3 H, H-27), 1.64 (d, $J_{5'',6''}$ = 6.2 Hz, 3 H, H-6″), 3.27 (dd, *J* = 13.5, 3.4 Hz, 1 H, H-18), 3.70 (d, *J* = 10.9 Hz, 1 H, H-23a), 3.76 (d, $J_{5'a,5'b}$ = 11.6 Hz, 1 H, H-5′a), 4.18 (dd, $J_{2',3'}$ = 9.2, $J_{3',4'}$ = 3.1 Hz, 1 H, H-3′), 4.25 (dd, *J* = 11.9, 4.3 Hz, 1 H, H-3), 4.29 (d, *J* = 11.0 Hz, 1 H, H-23b), 4.30 (t, $J_{3'',4''} = J_{4'',5''}$ = 9.2 Hz, 1 H, H-4″), 4.36 (m, 2 H, H-4′, H-5′b), 4.40 (dd, $J_{2',3'}$ = 8.9, $J_{1',2'}$ = 7.5 Hz, 1 H, H-2′), 4.47 (m, 1 H, H-5″), 4.57 (dd, $J_{3'',4''}$ = 9.4, $J_{2'',3''}$ = 3.3 Hz, 1 H, H-3″), 4.73 (dd, $J_{2'',3''}$ = 3.2, $J_{1'',2''}$ = 1.4 Hz, 1 H, H-2″), 4.99 (d, $J_{1',2'}$ = 7.2 Hz, 1 H, H-1′), 5.48 (m, 1 H, H-12), 5.92 (s, 1 H, H-1″) ppm. ^{13}C NMR ([D$_5$]pyridine): δ = 13.3 (C-24), 15.7 (C-25), 17.1 (C-26), 17.8 (C-6), 18.2 (C-6″), 23.3 (C-16), 23.4 (C-30), 23.5 (C-11), 25.8 (C-2), 25.8 (C-27), 27.9 (C-15), 30.6 (C-20), 32.4 (C-7), 32.8 (C-22), 32.9 (C-29), 33.8 (C-21), 36.5 (C-10), 38.3 (C-1), 39.4 (C-8), 41.6 (C-18), 41.8 (C-14), 43.1 (C-4), 46.0 (C-19), 46.3 (C-17), 47.1 (C-5), 47.8 (C-9), 63.8 (C-23), 65.6 (C-5′), 69.8 (C-5″), 71.6 (C-2″), 72.0 (C-3″), 72.6 (C-2′), 73.7 (C-4″), 73.8 (C-3′), 75.6 (C-4′), 82.0 (C-3), 103.0 (C-1″), 106.4 (C-1′), 122.2 (C-12), 144.5 (C-13), 180.0 (C-28) ppm. ESI-MS: *m*/*z* = 774 [M + Na + H]$^+$. $C_{41}H_{66}O_{12}$·3.2H_2O (808.62): calcd. C 60.90, H 9.03; found C 60.91, H 8.98.

Allyl Hederagenate 35: Allyl bromide (1.43 mL, 16.5 mmol, 2 equiv.) and potassium carbonate (2.48 g, 24.8 mmol, 3 equiv.) were added to a solution of hederagenin (see general remarks; 3.9 g, 8.3 mmol) in DMF (54 mL). The reaction mixture was heated to 50 °C for 5 h. After cooling, EtOAc was added and the organic layer was washed with 1 N HCl. The aqueous layer was then extracted with EtOAc (3×), and the combined organic layers washed with satd. $NaHCO_3$ (sat) and NaCl (sat). The dried solution (Na_2SO_4) was then evaporated under reduced pressure to give the crude product, which was purified by column chromatography (cyclohexane/EtOAc, 4:1 to 2:1) to give **35** (2.58 g, 61%) as a white foam. R_f = 0.25 (cyclohexane/EtOAc, 6:4). $[\alpha]_D$ = +60.1 (*c* = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 0.78 (s, 3 H, H-26), 0.85−2.07 (m, 22 H), 0.94 (s, 3 H, H-24), 0.95 (s, 3 H, H-29), 0.98 (s, 3 H, H-30), 1.00 (s, 3 H, H-25), 1.18 (s, 3 H, H-27), 2.93 (dd, *J* = 13.7, 4.0 Hz, 1 H, H-18), 3.48 (d, *J* = 10.3 Hz, 1 H, H-23a), 3.69 (dd, *J* = 8.5, 7.3 Hz, 1 H, H-3), 3.78 (d, *J* = 10.3 Hz, 1 H, H-23b), 4.58 (m, 2 H, CH_2CH=CH$_2$), 5.26 (dd, *J* = 10.4, 0.9 Hz, 1 H, CH$_2$CH=CH_2), 5.35 (m, 2 H, H-12, CH$_2$CH=CH_2), 5.94 (m, 1 H, CH$_2$CH=CH$_2$) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.3 (C-24), 15.7 (C-25), 17.0 (C-26), 18.5 (C-6), 23.0 (C-16), 23.3 (C-11), 23.6 (C-30), 25.9 (C-27), 26.7 (C-2), 27.6 (C-15), 30.7 (C-20), 32.4 (C-22), 32.5 (C-7), 33.1 (C-29), 33.8 (C-21), 36.9 (C-10), 38.1 (C-1), 39.3 (C-8), 41.3 (C-18), 41.7 (C-14), 41.8 (C-4), 45.8 (C-19), 46.7 (C-17), 47.6 (C-9), 49.8 (C-5), 64.8 (*C*H$_2$CH=CH$_2$), 72.2 (C-23), 76.9 (C-3), 117.7 (CH$_2$CH=*C*H$_2$), 122.3 (C-12), 132.5 (CH$_2$*C*H=CH$_2$), 143.6 (C-13), 177.4 (C-28) ppm. $C_{33}H_{52}O_4$ (512.77): calcd. C 77.30, H 10.22; found C 77.11, H 10.49.

Allyl 23-*O*-Benzoylhederagenate (36): Allyl hederagenate **35** (2.3 g, 4.5 mmol) was treated with benzoyl chloride in the same manner as that described for methyl 23-*O*-benzoylhederagenate (**29**). Purification by column chromatography (cyclohexane/EtOAc, 9:1) gave the desired product **36** (1.74 g, 63%). R_f = 0.60 (cyclohexane/EtOAc, 6:4) $[\alpha]_D$ = +17.3 (*c* = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 0.80 (s, 3 H, H-26), 0.85−2.07 (m, 22 H), 0.90 (s, 3 H, H-24), 0.95 (s, 3 H, H-29), 0.98 (s, 3 H, H-30), 1.02 (s, 3 H, H-25), 1.16 (s, 3 H, H-27), 2.94 (dd, *J* = 13.8, 4.0 Hz, 1 H, H-18), 3.55 (dd, *J* = 11.4, 5.5 Hz, 1 H, H-3), 4.05 (d, *J* = 11.4 Hz, 1 H, H-23a), 4.57 (m, 3 H, H-23b, CH_2CH=CH$_2$), 5.26 (dd, *J* = 10.5, 1.3 Hz, 1 H, CH$_2$CH=CH_2), 5.35 (m, 1 H, H-12), 5.37 (m, 1 H, CH$_2$CH=CH_2), 5.96 (m, 1 H, CH$_2$CH=CH$_2$), 7.51 (t, *J* = 8.0 Hz, 2 H, Ar-H), 7.63 (t, *J* = 7.4 Hz, 1 H, Ar-H), 8.10 (dd, *J* = 8.4, 1.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 12.0 (C-24), 15.8 (C-25), 17.0 (C-26), 18.2 (C-6), 23.0 (C-16), 23.4 (C-11), 23.6 (C-30), 25.5 (C-27), 26.1 (C-2), 27.6 (C-15), 30.7 (C-20), 32.4 (C-22), 32.5 (C-7), 33.1 (C-29), 33.9 (C-21), 36.8 (C-10), 38.4 (C-1), 39.3 (C-8), 41.4 (C-18), 41.6 (C-14), 42.5 (C-4), 45.8 (C-19), 46.7 (C-17), 48.0 (C-9), 48.3 (C-5), 64.8 (*C*H$_2$CH=CH$_2$), 66.7 (C-23), 72.4 (C-3), 117.7 (CH$_2$CH=*C*H$_2$), 122.3 (C-12), 128.5 (CH), 129.5 (CH), 130.1 (C), 132.5 (CH$_2$*C*H=CH$_2$), 133.1 (CH), 143.6 (C-13), 166.8 (CO), 177.3 (C-28) ppm. $C_{40}H_{56}O_5$ (616.88): calcd. C 77.88, H 9.15; found C 77.59, H 9.34.

Allyl 3-*O*-[2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-arabinopyranosyl]-23-*O*-benzoylhederagenate (37): This compound was prepared in the same manner as that described for **31** using allyl hederagenate **36** (0.150 g, 0.24 mmol) and the trichloroacetimidate **24** (0.468 g, 0.48 mmol, 2 equiv.) in propionitrile at −78 °C. The crude residue was purified by column chromatography (toluene/EtOAc, 99:1 to 39:1) to give a mixture of anomeric products that were separated by HPLC (100% acetonitrile) to give the desired saponoside **37** (0.192 g, 56%) as a white foam and the β anomer **38** (0.075 g, 22%).

Compound 37 (α anomer): R_f = 0.50 (toluene/EtOAc, 9:1). $[\alpha]_D$ = +90.2 (*c* = 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 0.79 (s, 3 H, H-26), 0.83 (s, 3 H, H-24), 0.95 (s, 3 H, H-29), 0.98 (s, 3 H, H-30), 1.02 (s, 3 H, H-25), 1.05−2.10 (m, 22 H), 1.11 (s, 3 H, H-27), 1.33 (d,

$J_{5'',6''}$ = 5.9 Hz, 3 H, H-6″), 2.93 (dd, J = 13.7, 3.6 Hz, 1 H, H-18), 3.72 (dd, J = 11.6, 4.3 Hz, 1 H, H-3), 3.88 (dd, $J_{5'a,5'b}$ = 11.8, $J_{4',5'a}$ = 2.4 Hz, 1 H, H-5′a), 4.17 (d, J = 11.4 Hz, 1 H, H-23a), 4.32 (dd, $J_{5'a,5'b}$ = 11.9, $J_{4',5'b}$ = 6.1 Hz, 1 H, H-5′b), 4.39 (dd, $J_{2',3'}$ = 6.3, $J_{1',2'}$ = 4.7 Hz, 1 H, H-2′), 4.45 (d, J = 11.7 Hz, 1 H, H-23b), 4.49 (m, 1 H, H-5″), 4.58 (m, 2 H, CH_2CH=CH$_2$), 4.91 (d, $J_{1',2'}$ = 4.0 Hz, 1 H, H-1′), 5.26 (d, J = 10.5 Hz, 1 H, CH$_2$CH=CH_2), 5.37 (m, 3 H, H-12, CH$_2$CH=CH_2), 5.43 (s, 1 H, H-1″), 5.60 (dd, $J_{2',3'}$ = 6.6, $J_{3',4'}$ = 3.3 Hz, 1 H, H-3′), 5.64 (t, $J_{4'',5''}$ = $J_{3'',4''}$ = 10.1 Hz, 1 H, H-4″), 5.68 (m, 1 H, H-4′), 5.78 (m, 1 H, H-2″), 5.89 (dd, $J_{3'',4''}$ = 10.2, $J_{2'',3''}$ = 3.3 Hz, 1 H, H-3″), 5.95 (m, 1 H, CH$_2$CH=CH$_2$), 7.22−7.72 (m, 20 H, Ar-H), 7.99 (d, J = 7.7 Hz, 2 H, Ar-H), 8.05 (d, J = 7.7 Hz, 2 H, Ar-H), 8.1 (t, J = 7.6 Hz, 6 H, Ar-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 12.8 (C-24), 15.8 (C-25), 17.0 (C-26), 17.5 (C-6″), 18.0 (C-6), 23.0 (C-16), 23.4 (C-11), 23.6 (C-30), 25.4 (C-27), 25.5 (C-2), 27.5 (C-15), 30.7 (C-20), 32.4 (C-22), 32.5 (C-7), 33.1 (C-29), 33.9 (C-21), 36.5 (C-10), 38.5 (C-1), 39.3 (C-8), 41.4 (C-18), 41.6 (C-14), 42.4 (C-4), 45.8 (C-19), 46.7 (C-17), 48.0 (C-9), 48.2 (C-5), 60.3 (C-5′), 64.8 (CH_2CH=CH$_2$), 65.4 (C-23), 67.8 (C-4′, C-5″), 69.1 (C-3″), 70.7 (C-2″, C-3′), 71.8 (C-4″), 75.1 (C-2′), 82.2 (C-3), 98.6 (C-1″), 102.5 (C-1′), 117.7 (CH$_2$CH=CH_2), 122.3 (C-12), 128.0 (CH), 128.2 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 129.1 (C), 129.2 (C), 129.4 (C), 129.5 (CH), 129.6 (C), 129.7 (CH), 129.8 (CH), 129.9 (CH), 130.3 (C), 132.5 (CH$_2$CH=CH$_2$), 132.8 (CH), 133.0 (CH), 133.1 (CH), 133.2 (CH), 133.4 (CH), 143.7 (C-13), 164.8 (CO), 165.3 (CO), 165.4 (CO), 165.5 (CO), 165.8 (CO), 165.9 (CO), 177.3 (C-28) ppm. $C_{86}H_{94}O_{18}$·0.2 EtOAc (1433.30): calcd. C 72.74, H 6.72; found C 72.41, H 6.92.

Compound 38 (β anomer): R_f = 0.46 (toluene/EtOAc, 9:1). $[\alpha]_D$ = +153.8 (c = 1, CHCl$_3$). ^{1}H NMR (CDCl$_3$): δ = 0.84 (s, 3 H, H-26), 0.95 (s, 3 H, H-29), 0.99 (s, 3 H, H-30), 1.05−2.20 (m, 22 H), 1.11 (s, 3 H, H-27), 1.13 (s, 3 H, H-25), 1.19 (s, 3 H, H-24), 1.41 (d, $J_{5'',6''}$ = 6.3 Hz, 3 H, H-6″), 2.95 (dd, J = 13.8, 3.8 Hz, 1 H, H-18), 3.90 (dd, $J_{5'a,5'b}$ = 13.0, $J_{4',5'a}$ = 1.6 Hz, 1 H, H-5′a), 4.00 (dd, J = 11.3, 3.9 Hz, 1 H, H-3), 4.30 (d, $J_{5'a,5'b}$ = 12.7 Hz, 1 H, H-5′b), 4.38 (m, 1 H, H-5″), 4.48 (s, 2 H, H-23), 4.55 (dd, $J_{2',3'}$ = 10.5, $J_{1',2'}$ = 3.7 Hz, 1 H, H-2′), 4.61 (m, 2 H, CH_2CH=CH$_2$), 5.28 (dd, J = 10.4, 1.2 Hz, 1 H, CH$_2$CH=CH_2), 5.37 (m, 1 H, H-12), 5.39 (m, 1 H, CH$_2$CH=CH_2), 5.41 (s, 1 H, H-1″), 5.43 (d, $J_{1',2'}$ = 3.7 Hz, 1 H, H-1′), 5.55 (dd, $J_{2'',3''}$ = 3.1, $J_{1'',2''}$ = 1.8 Hz, 1 H, H-2″), 5.70 (t, $J_{3'',4''}$ = $J_{4'',5''}$ = 9.9 Hz, 1 H, H-4″), 5.76 (dd, $J_{2',3'}$ = 10.4, $J_{3',4'}$ = 3.3 Hz, 1 H, H-3′), 5.85 (m, 1 H, H-4′), 5.93 (dd, $J_{3'',4''}$ = 10.0, $J_{2'',3''}$ = 3.3 Hz, 1 H, H-3″), 5.98 (m, 1 H, CH$_2$CH=CH$_2$), 7.24−7.68 (m, 18 H, Ar-H), 7.82 (d, J = 7.3 Hz, 2 H, Ar-H), 8.02 (m, 8 H, Ar-H), 8.12 (d, J = 7.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 13.3 (C-24), 15.8 (C-25), 17.1 (C-26), 17.7 (C-6″), 18.1 (C-6), 21.4 (C-2), 23.0 (C-16), 23.5 (C-11), 23.6 (C-30), 25.4 (C-27), 27.6 (C-15), 30.7 (C-20), 32.3 (C-22), 32.5 (C-7), 33.1 (C-29), 33.8 (C-21), 36.8 (C-10), 38.1 (C-1), 39.4 (C-8), 41.4 (C-18), 41.7 (C-14), 42.3 (C-4), 45.8 (C-19), 46.7 (C-17), 48.1 (C-9), 48.3 (C-5), 60.9 (C-5′), 64.8 (CH_2CH=CH$_2$), 65.8 (C-23), 67.3 (C-5″), 69.0 (C-3″), 70.2 (C-3′), 70.3 (C-4′), 70.7 (C-2″), 71.9 (C-4″), 73.9 (C-2′), 76.4 (C-3), 94.6 (C-1′), 98.8 (C-1″), 117.8 (CH$_2$CH=CH_2), 122.2 (C-12), 128.2 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 129.2 (C), 129.3 (C), 129.4 (C), 129.5 (CH), 129.6 (CH), 129.7 (CH), 130.4 (C), 132.5 (CH$_2$CH=CH$_2$), 133.0 (CH), 133.2 (CH), 133.4 (CH), 133.5 (CH), 143.9 (C-13), 164.9 (CO), 165.0 (CO), 165.6 (CO), 165.7 (CO), 166.0 (CO), 177.3 (C-28) ppm. ESI-MS: m/z = 1438 [M + Na]$^+$.

3-*O*-[α-L-Rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl]hederagenin (α-Hederin) (1): This compound was prepared from saponoside **37** (0.203 g, 0.14 mmol) by treatment with 3% KOH in methanol in the same manner as that described for **4**. Neutralization of the reaction mixture with Amberlite IR 120 (H$^+$ form), filtration, and evaporation gave the crude allyl ester, which was used without purification in the next step. Tetrakis(triphenylphosphane)palladium(0) (0.050 g, 0.043 mmol, 0.3 equiv.) was added to a mixture of the crude allyl ester, triphenylphosphane (0.023 g, 0.086 mmol, 0.6 equiv.), and pyrrolidine (24 μL, 0.28 mmol, 2 equiv.) in THF (1 mL) at room temp. The reaction mixture was stirred overnight or until TLC indicated the total disappearance of the starting material. Evaporation of the solvent and purification by column chromatography (CH$_2$Cl$_2$/MeOH, 19:1) gave α-hederin **1** (0.096 g, 91%) as an amorphous white solid that was identical to an authentic sample of α-hederin (TLC). Spectral identification was performed in [D$_5$]pyridine and was in accordance with published data.[31]

[1] K. Hostettmann, A. Marston, *Saponins*, Cambridge University Press, Cambridge, UK, **1995**.
[2] K. Hostettmann, *Helv. Chim. Acta* **1980**, *63*, 606−609.
[3] J. Quetin-Leclercq, R. Elias, G. Balansard, R. Bassler, L. Angenot, *Planta Med.* **1992**, *58*, 279−281.
[4] [4a] A. Favel, M. D. Steinmetz, E. Ollivier, R. Elias, P. Régli, G. Balansard, *Planta Med.* **1992**, *58*, 279−281. [4b] V. Mshvildadze, A. Favel, F. Delmas, R. Elias, R. Faure, G. Dekanosidze, E. Kemertelidze, G. Balansard, *Pharmazie* **2000**, *55*, 325−326. [4c] O. Ridoux, C. Di Giorgio, F. Delmas, R. Elias, V. Mshvildadze, G. Dekanosidze, E. Kemertelidze, G. Balansard, P. Timon-David, *Phytother. Res.* **2001**, *15*, 298−301.
[5] [5a] S. S. Muthu Kumara, B. T. Kwong Huat, *Planta Med.* **2001**, *67*, 29−32. [5b] H.-J. Park, S.-H. Kwon, J.-H. Lee, K.-H. Lee, K. Miyamoto, K.-T. Lee, *Planta Med.* **2001**, *67*, 118−121. [5c] C. Barthoneuf, E. Debiton, V. Mshvildadze, E. Kemertelidze, G. Balansard, *Planta Med.* **2002**, *68*, 672−675.
[6] D. W. Li, E. B. Lee, S. S. Kang, J. E. Hyun, W. K. Whang, *Chem. Pharm. Bull.* **2002**, *50*, 900−903.
[7] D. W. Li, J. E. Hyun, C. S. Jeong, Y. S. Kim, E. B. Lee, *Biol. Pharm. Bull.* **2003**, *26*, 429−433.
[8] E. Schlösser, G. Wulff, *Z. Naturforsch., Teil B* **1969**, *24*, 1284−1290.
[9] L. Voutquenne, C. Lavaud, G. Massiot, L. Le Men-Olivier, *Pharmaceutical Biology* **2002**, *40*, 253−262.
[10] [10a] M. Takechi, C. Uno, Y. Tanaka, *Phytochemistry* **1996**, *41*, 121−123. [10b] K. Oda, H. Matsuda, T. Murakami, S. Katayama, T. Ohgitani, M. Yoshikawa, *J. Biol. Chem.* **2000**, *381*, 67−74.
[11] W. Seebacher, E. Haslinger, K. Rauchensteiner, J. Jurenitsch, A. Presser, R. Weis, *Monatsh. Chem.* **1999**, *130*, 887−897.
[12] W. Seebacher, R. Weis, J. Jurenitsch, K. Rauchensteiner, E. Haslinger, *Monatsh. Chem.* **2000**, *131*, 985−996.
[13] [13a] R. Suhr, M. Lahmann, S. Oscarson, J. Thiem, *Eur. J. Org. Chem.* **2003**, 4003−4011. [13b] B. Yu, H. Tao, *J. Org. Chem.* **2002**, *67*, 9099−9102. [13c] B. Yu, B. Li, G. Xing, Y. Hui, *J. Comb. Chem.* **2001**, *3*, 404−406. [13d] S. Deng, B. Yu, Y. Lou, Y. Hui, *J. Org. Chem.* **1999**, *64*, 202−208. [13e] P. L. Fuchs, C. Guo, *Tetrahederon Lett.* **1998**, *39*, 1099−1102.
[14] [14a] J. Sun, X. Han, B. Yu, *Carbohydr. Res.* **2003**, *338*, 827−833. [14b] W. Seebacher, R. Weis, J. Jurenitsch, K. Rauchensteiner, E. Haslinger, *Monatsh. Chem.* **1999**, *130*, 1383−1391. [14c] B. Yu, J. Xie, S. Deng, Y. Hui, *J. Am. Chem. Soc.* **1999**, *121*, 12196−12197.
[15] N. Ullah, W. Seebacher, R. Weis, J. Jurenitsch, K. Rauchensteiner, E. Haslinger, *Monatsh. Chem.* **2000**, *131*, 787−794.
[16] A. Lipták, Z. Szurmai, P. Nánási, *Tetrahedron* **1982**, *38*, 3489−3497.
[17] S. Kamiya, S. Esaki, R. Tanaka, *Agric. Biol. Chem.* **1984**, *48*, 1353−1355.

[18] S. Kamiya, S. Esaki, R. Tanaka, *Agric. Biol. Chem.* **1985**, *49*, 55−62.
[19] S. Kamiya, S. Esaki, R. Sano, C. Yamaguchi, *Agric. Biol. Chem.* **1986**, *50*, 2147−2149.
[20] [20a] A. van Steijn, J. P. Kamerling, J. F. G. Vliegenthart, *Carbohydr. Res.* **1992**, *225*, 229−245. [20b] H. Akita, K. Kurashima, T. Nakamura, K. Kato, *Tetrahedron: Asymmetry* **1999**, *10*, 2429−2439. [20c] S. Cherif, M. R. Leach, D. B. Williams, C. Monneret, *Bioorg. Med. Chem. Lett.* **2002**, *12*, 1237−1240.
[21] [21a] A. Lubineau, C. Augé, N. Le Goff, C. Le Narvor, *Carbohydr. Res.* **1998**, *305*, 501−509. [21b] M. Tsuzuki, T. Tsuchiya, *Carbohydr. Res.* **1998**, *311*, 11−24.
[22] T. Sivakumaran, J. K. N. Jones, *Can. J. Chem.* **1967**, *45*, 2493−2500.
[23] T. Ziegler, F. Bien, C. Jurisch, *Tetrahedron: Asymmetry* **1998**, *9*, 765−780.
[24] R. R. Schmidt, K.-H. Jung, in *Preparative Carbohydrate Chemistry*, Marcel Dekker, New York, **1997**, 283−312.
[25] R. R. Schmidt, M. Behrendt, A. Toepfer, *Synlett* **1990**, 694−696.
[26] F. Elsinger, J. Schreiber, A. Eschenmoser, *Helv. Chim. Acta* **1960**, *43*, 113−118.
[27] The benzoylated allyl ester saponins were fully characterized by 1D and 2D NMR spectroscopy techniques; they were identical in all respects to the corresponding benzoylated methyl ester saponins, except for minor differences resulting from the presence of the allyl group and the absence of the methyl ester.
[28] NMR spectral analysis was in agreement with the values given in: K. Tori, S. Seo, A. Shimaoka, Y. Tomita, *Tetrahedron Lett.* **1974**, *48*, 4227−4230.
[29] The plant extract was given to our laboratory by Professor G. Balansard.
[30] L. Jayasinghe, H. Shimada, N. Hara, Y. Fujimoto, *Phytochemistry* **1995**, *40*, 891−897.
[31] R. P. Thapliyal, R. P. Bahuguna, *Phytochemistry* **1993**, *33*, 671−673.

Received November 13, 2003

