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Synthesis of two bidesmosidic ursolic acid saponins bearing a 2,3-branched trisaccharide residue

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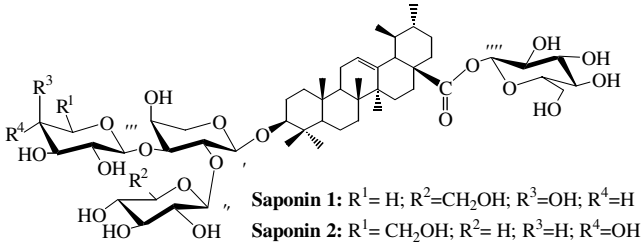
Abstract—The focus of this work was on the synthesis of two bidesmosidic ursolic acid saponins bearing a 2,3-branched trisaccharide residue. Therefore, 3-*O*-{[β-D-glucopyranosyl-(1→2)]-[α-L-arabinopyranosyl-(1→3)]-α-L-arabinopyranosyl}ursolic acid-28-*O*-[β-D-glucopyranosyl] ester **1** was concisely synthesized by two strategies in 22% and 41% overall yield, respectively, and another congener 3-*O*-{[β-D-xylopyranosyl-(1→2)]-[β-D-glucopyranosyl-(1→3)]-α-L-arabinopyranosyl}ursolic acid-28-*O*-[β-D-glucopyranosyl] ester **2** was also efficiently prepared in 81% overall yield. The ^{1}H NMR and ^{13}C NMR signals of saponin **2** are all consistent with those reported for the natural product.

Keywords: Ursolic acid; Saponin; Glycosylation; Synthesis

1. Introduction

Ursolic acid, a pentacyclic triterpene isolated from many traditional medicinal plants, has been reported to possess a wide range of pharmacological activities, including anti-tumor,[1–3] anti-inflammatory,[4] and anti-HIV.[5] It is also one of the most promising chemopreventive agents for cancer.[6] Attracted by these interesting bioactivities, several research groups reported on the synthesis of the acid-based derivatives for developing more potent compounds.[7–9] Interestingly, the naturally occurring ursolic acid saponins, the glycosidic derivatives of ursolic acid, are very rare. With the increasing recognition of the importance of the saccharide part in saponin bioactivities,[10–12] we find ourselves more interested in how the sugar moiety affects the bioactivities and pharmacokinetic properties of ursolic acid. Therefore, a project was initiated to carry out the synthesis of ursolic acid saponins. We were first attracted by the two naturally occurring bidesmosidic ursolic acid saponins. Saponin **1**, 3-*O*-{[β-D-glucopyranosyl-(1→2)]-[α-L-arabinopyranosyl-(1→3)]-α-L-arabinopyranosyl}ursolic acid-28-*O*-[β-D-glucopyranosyl] ester, was isolated from a medicinal plant *Fagonia indica*.[13] And another congener saponin **2**, 3-*O*-{[β-D-xylopyranosyl-(1→2)]-[β-D-glucopyranosyl-(1→3)]-α-L-arabinopyranosyl}ursolic acid-28-*O*-[β-D-glucopyranosyl] ester, was isolated from *Fagonia arabica*[14] and *Aralia decaisneana*.[15] The 2,3-branched oligosaccharide chain represents a typical structure in natural bioactive saponins[16–18] and its introduction to an aglycone is the crucial step to the synthesis. Herein, we report the synthesis of the two saponins.



Saponin 1: R^1= H; R^2=CH_2OH; R^3=OH; R^4=H
Saponin 2: R^1= CH_2OH; R^2= H; R^3=H; R^4=OH

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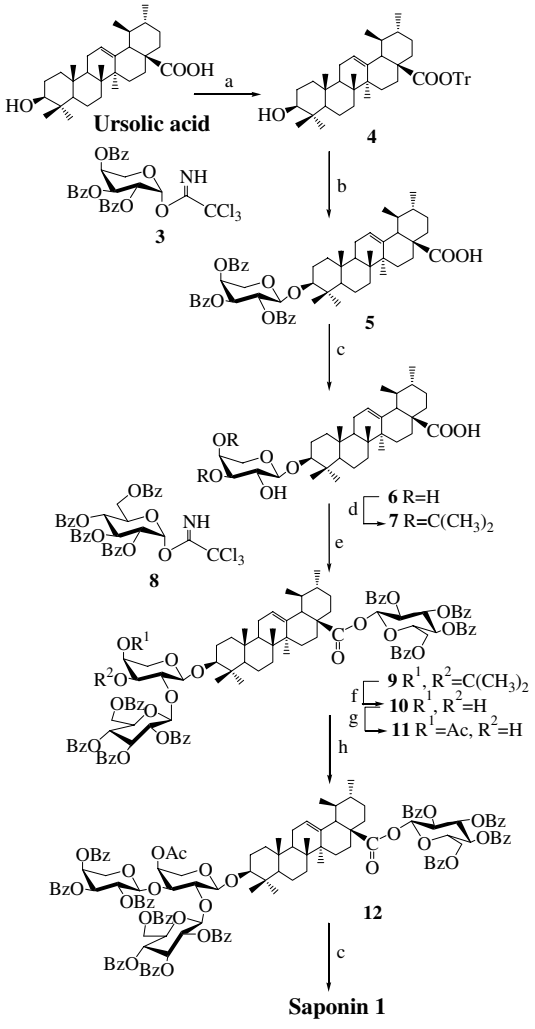
2. Results and discussion

Saponins **1** and **2** are characterized by the attachment of a 2,3-branched trisaccharide to the C-3 position and the glucose to the C-28 position of the ursolic acid aglycone. It has been reported that, in convergent glycosylation fashion, an α,β mixture was unavoidable due to the absence of C-2 neighboring-group participation[16] when a 2,3-branched saccharide donor was incorporated with an aglycone acceptor. In stepwise glycosylation, however, another strategy for saponin synthesis, the resulting saponin can be obtained stereospecifically.[19] Herein, we planned to adopt the approach of stepwise glycosylation to the target molecules. The synthetic access to saponin **1** was first attempted as in Scheme 1.

Starting from ursolic acid, after protection of the 28-CO_2H with Tr,[20] compound **4** was then glycosylated with the benzoylated arabinopyranosyl donor **3**[21] at −60 °C, followed by deprotection of the Tr[20] group by warming the solution to room temperature for another 30 min to provide the key intermediate **5** in exclusively the 1,2-*trans* glycosidic linkage. Debenzoylation with NaOMe gave triol **6**, which was subjected to DMP (2,2-dimethoxypropane) in the presence of PPTs to afford **7** in an excellent yield (91%). The simultaneous glycosylation of the 2′-OH and 28-CO_2H groups in **7** with the benzoylated glucopyranosyl trichloroacetimidate **8**[21] was successfully achieved in the presence of Me_3SiOTf to give the desired **9** (80%). Removal of the acetonide isopropylidene group afforded the 3,4-diol **10** in good yield.



Scheme 1. Reagents and conditions: (a) TrCl, DBU, reflux, 82%; (b) **3**, Me_3SiOTf (0.3 equiv), −60 °C→rt; (c) CH_3ONa, rt, 96% for **6** two steps; 99% for **1**; (d) PPTs, $(CH_3)_2C(OCH_3)_2$, rt, 12 h, 91%; (e) **8**, Me_3SiOTf (0.1 equiv), 0 °C→rt, 80%; (f) 80% AcOH, 70 °C, 94%; (g) (i) *p*-TsOH·H_2O, $CH_3C(OCH_2CH_3)_3$, rt, (ii) 50%AcOH, 70 °C, 86%; (h) $BF_3{\cdot}Et_2O$, −40 °C→rt, 47%.

The next task was the introduction of an arabinopyranosyl residue to the 3′-OH of **10**. It is well known that the equatorial 3′-OH is more reactive than the axial 4′-OH in many pyranosides,[22,23] and so an attempt at selective glycosylation of the 3′-OH of the acceptor **10** with the acetylated arabinopyranosyl donor was made. However, the ^{13}C–^{1}H HMBC spectral data showed that glycosylation had taken place at the 4′-OH. Apparently, this unusual regioselectivity resulted from the diminished reactivity of the 3′-OH due to the introduction of the bulky benzoyled glucopyranosyl part at 2′-OH. Therefore, regioselective protection[24] of the 4′-OH group in **10** with an acetyl group was first performed, to provide the key receptor **11** in 86% yield. Next the 3′-OH glycosylation with benzoylated arabinopyranosyl donor **3** was attempted in the following process. The glycosylation reaction proved difficult. After investigating a variety of conditions, including arabinopyranosyl donors, promoters, reaction temperature, and reaction time, we found that compound **12** could be generated using $BF_3{\cdot}Et_2O$ as the catalyst at −40 °C for 12 h in 47% yield. When the reaction temperature was elevated from −40 to −20 °C, only a trace amount of the desired product was obtained, meanwhile, a large amount of acetyl migration product (acetyl group migrating from 4′-OH to 3′-OH in **11**) was obtained.

Four anomeric proton signals at δ 4.27 (J 7.3 Hz, H-1′), 4.54 (J 6.4 Hz, H-1‴), 4.71 (J 7.3 Hz, H-1″), 5.88 (J 8.7 Hz, H-1⁗) and carbon signals at δ 104.1 (C-1′), 100.4 (C-1″, C-1‴), 92.0 (C-1⁗) in the ^{1}H NMR and ^{13}C NMR spectra of **12** indicated a β-linkage to the glucopyranosyl residue and an α-linkage to the arabinopyranosyl residue. The HMBC cross peaks between H-1″ (glucose)→C-2′ (inner arabinose) and H-1‴ (terminal arabinose)→C-3′ (inner arabinose) prove the interglycosidic linkage of glucose at position C-2′ and terminal arabinose at position C-3′ of the inner arabinose. The target saponin **1** was finally obtained by removal of all the protective groups with NaOMe in 22% overall yield. The low yield was attributed to the difficulty of glycosylation of the highly hindered 3′-OH in acceptor **11** at the later stage. To our surprise, we found that the ^{1}H NMR

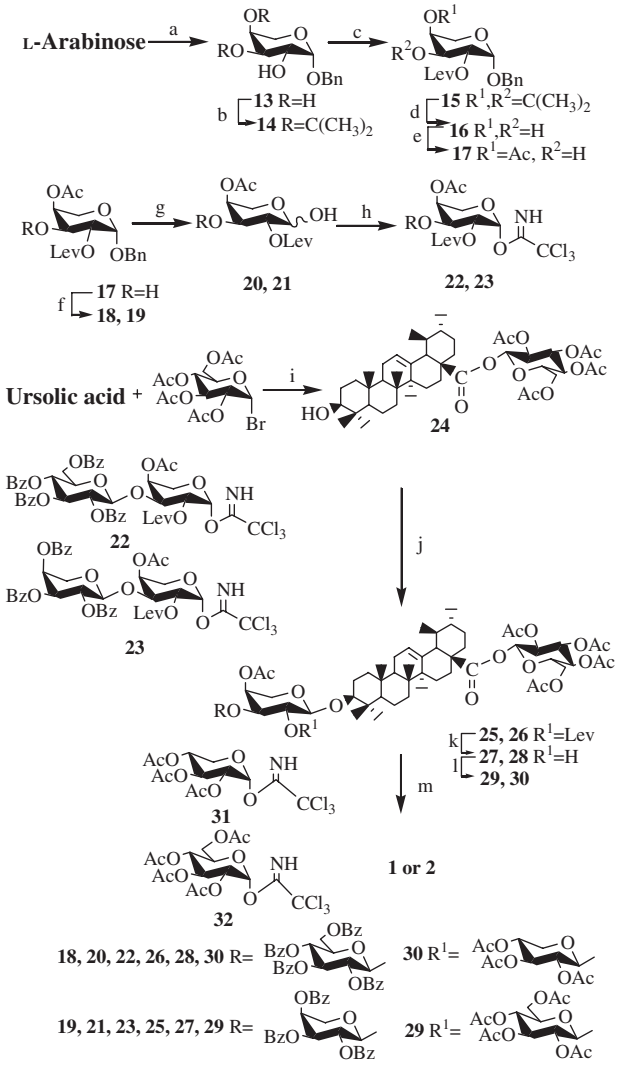
and ^{13}C NMR signals of saponin **1** are not consistent with those in the literature.[13]

To further prove the structure of saponin **1** and improve the overall yield, we intended to adopt an alternative process to synthesize saponin **1** and its congener saponin **2**, that is, the (1→3)-disaccharide residue was the first to be coupled with the 3′-OH of ursolic acid stereoselectively, and then another monosaccharide was to be introduced to the 2′-OH. Such a strategy could ensure the stereoselective formation of the desired 1,2-*trans* 3-*O*-glycosidic linkages in the aglycone and also avoid the difficulty in the glycosylation of 3′-OH in the inner arabinose residue. The corresponding retrosynthetic analysis is shown in Scheme 2, and the synthetic route to saponin **1** and **2** is described in Scheme 3.

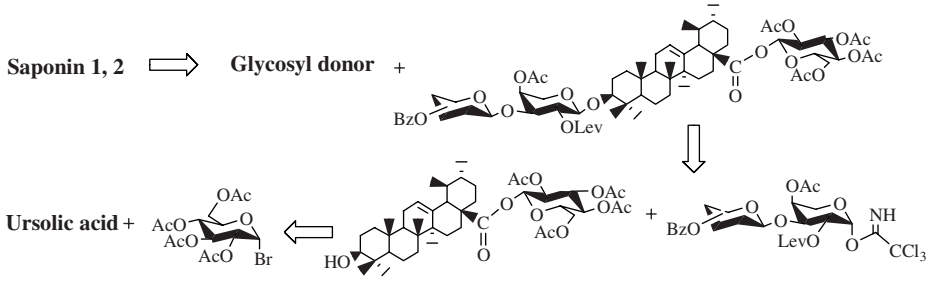
The key monosaccharide **17** was prepared from L-arabinose in five steps. L-Arabinose was first treated with BnOH and $BF_3{\cdot}Et_2O$ to give benzyl β-L-arabinopyranoside (**13**), which was isopropylidenated to provide **14** with the 2′-OH free. To obtain a distinguishable 2-*O*-protecting group, allowing selective cleavage in the presence of an acyl protecting group and ensuring the stereoselectivity in forming the 1,2-*trans* glycosidic linkages, herein, the Lev[25] group was chosen and introduced by the treatment of **14** with levulinic acid, DCC-DMAP to obtain **15** in quantitative yield. Then the removal of the isopropylidene group from **15** with 80% AcOH readily produced the 3,4-diol **16** in 93% yield, which was acetylated regioselectively at 4-OH by using the same procedure as for **10**, providing acceptor **17** with 3′-OH free in 94% yield.

The (1→3)-β-disaccharides **18** and **19** were obtained by glycosylation of **17** with benzoylated glucopyranosyl donor **8** and benzoylated arabinopyranosyl donor **3**, respectively, under standard conditions in good yield. The anomeric benzyl groups of **18** and **19** were hydrogenolyzed under Pd–C (10%) for 12 h to afford hemiacetals **20** and **21**, which were then converted into the corresponding trichloroacetimidate donors **22** and **23**.

The receptor **24** was first prepared in 99% yield by selective glycosylation of the 28-CO_2H group in the ursolic acid aglycone with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide[26] under phase-transfer condi-



Scheme 3. Reagents and conditions: (a) BnOH, $BF_3{\cdot}Et_2O$, 95 °C, 46%; (b) DMP, *p*-TsOH·H_2O, rt, 12 h, 79%; (c) DCC, DMAP, rt, 12 h, quant.; (d) 70% AcOH, 70 °C, 93%; (e) (i) $CH_3C(OCH_2CH_3)_3$, *p*-TsOH·H_2O, rt, 12 h; (ii) 80% AcOH, 70 °C, 94%; (f) Me_3SiOTf (0.1 equiv), CH_2Cl_2, −20 °C, 79% for **18**, 88% for **19**; (g) Pd–C (10%), rt, 81% for **20**, 88% for **21**; (h) CCl_3CN, DBU, rt, 71% for **22**, 57% for **23**; (i) Bu_4NBr, CH_2Cl_2–H_2O, K_2CO_3, 99%; (j) **22** or **23**, Me_3SiOTf (0.2 equiv), CH_2Cl_2, −20 °C, 88% for **25**, 96% for **26**; (k) NH_2NH_2–HOAc, CH_2Cl_2–CH_3OH, 91% for **27**, 90% for **28**; (l) Me_3SiOTf (0.1 equiv), −40 °C, 12 h, 53% for **29**, 97% for **30**; (m) NaOMe–MeOH, 98% for **1**, 98% for **2**.



Scheme 2. Retrosynthetic analysis of saponins **1** and **2**.

tions. Then coupling **24** with donors **22** and **23**, respectively, in the presence of Me_3SiOTf was performed to provide the expected products **25** and **26** in good yield and uniquely α-linked. Removal of the Lev group of **25** and **26** with NH_2NH_2–HOAc generated acceptors **27** and **28** with a free 2′-OH.

For introducing another sugar residue to the 2′-OH, the acceptor **27** was first glycosylated with benzoylated glucopyranosyl trichloroacetimidate **8** under standard conditions, however, this led to no reaction. This problem is probably due to the fact that 2′-OH of the arabinopyranosyl residue was surrounded by the rigid triterpene ring and the bulky benzoylated arabinopyranosyl part, and the high steric hindrance further decreased the reactivity of 2′-OH. On the basis of this above analysis, the donor was changed to the smaller acetylated glucopyranosyl trichloroacetimidate **32**.[27] And the coupling of the hindered 2′-OH of **27** with the acetylated glucopyranosyl donor under 'inverse addition' conditions[28] was then performed to give a satisfactory yield of the desired compound **29** (53%). Glycosylation of **28** with the acetylated xylopyranosyl trichloroacetimidate[29] under the same conditions gave **30** in excellent (97%) yield. The striking difference between the glycosylation yields is due to that the larger six-carbon glucopyranose has more difficultly accessing the 2′-OH compared with that of the five-carbon xylopyranose or the 6-deoxgenated six-carbon rhamnopyranose.[17] Deprotection of **29** with NaOMe gave the target saponin **1**, once again in 41% overall yield (better than 22%) and with exactly the same spectral data as those of the product synthesized above, indicating that the structure of the synthetic saponin **1** is correct. More significantly, the deprotection of **30** gave the target **2** in 81% overall yield, and its ^1H NMR and ^{13}C NMR signals are all consistent with those reported for the natural product.[14,15]

In conclusion, a concise and effective procedure has been successfully developed for the synthesis of bidesmosidic ursolic acid saponins bearing a 2,3-branched oligosaccharide moieties. The result of the present investigation should be of value in the synthesis of structural analogs.

3. Experimental

3.1. General methods

Solvents were purified conventionally. Thin-layer chromatography (TLC) was performed on precoated Merck silica gel 60 F_{254} plates. Flash column chromatography was performed on silica gel (200–300 mesh, Qingdao, China). Optical rotations were determined with a Perkin–Elmer Model 241 MC polarimeter. ^1H NMR and ^{13}C NMR spectra were taken on a Jeol JNM-ECP 600 spectrometer with tetramethylsilane (Me_4Si) as the internal standard, and chemical shifts are recorded in δ values. Mass spectra were recorded on a Q-TOF Global mass spectrometer.

3.2. Trityl ursolic ester (4)

To a suspension of ursolic acid (0.611 g, 1.34 mmol) in THF (15 mL) were added DBU (0.32 mL, 2.14 mmol) and TrCl (0.517 g, 1.85 mmol). The mixture was stirred at reflux for 16 h. Removal of solvent afforded a residue that was subjected to column chromatography (5:1 petroleum ether–EtOAc) to give **4** as a yellow solid (0.766 g, 82%): R_f 0.50 (3:1 petroleum ether–EtOAc); ^1H NMR ($CDCl_3$): δ 7.20–7.40 (m, 15H, Ph × 3), 5.21 (t, *J* 3.3 Hz, 1H, H-12), 3.19–3.21 (m, 1H, H-3), 2.23 (d, *J* 11.4 Hz, 1H, H-18), 2.04 (td, *J* 13.6, 4.7 Hz, 1H), 1.05, 0.97, 0.88, 0.78, 0.36 (s each, 3H each, Me × 5), 0.94 (d, *J* 6.2 Hz, 3H), 0.83 (d, *J* 6.6 Hz, 3H), 0.67 (d, *J* 11.0 Hz, 1H, H-5).

3.3. Ursolic acid-3-yl α-L-arabinopyranoside (6)

To a mixture of compound **4** (1.06 g, 1.52 mmol), **3** (1.20 g, 1.98 mmol), and powdered 4 Å molecular sieves in dried CH_2Cl_2 (10 mL) at −60 °C was added Me_3SiOTf (53 μL, 0.15 mmol). After stirring at −60 °C for 0.5 h and at rt for 0.5 h, the reaction was quenched with Et_3N. The solid was then filtered off. The filtrate was concentrated under vacuum to give a yellow oil, which was purified by column chromatography (4:1 petroleum ether–EtOAc) to give compound **5** as a crude. Compound **5** was dissolved in MeOH–CH_2Cl_2 (2:1, 21 mL), and then NaOMe (100 mg, 50%) was added. After stirring at rt for 4 h, the solution was neutralized with ion-exchange resin (H^+), filtered, and concentrated. The residue was purified by column chromatography (20:1→2:1 $CHCl_3$–MeOH) to afford **6** as a white solid (0.86 g, 96%): R_f 0.50 (10:1 $CHCl_3$–MeOH); $[\alpha]_D^{20}$ +43.5 (*c* 0.17, $CHCl_3$); ^1H NMR (CD_3OD): δ 5.21 (t, *J* 3.7 Hz, 1H, H-12), 4.26 (d, *J* 6.9 Hz, 1H, H-1′), 3.79–3.83 (m, 2H), 3.49–3.57 (m, 3H), 3.13 (dd, *J* 11.4, 4.1 Hz, 1H, H-3), 2.19 (d, *J* 11.4 Hz, 1H, H-18), 1.11, 1.01, 0.96, 0.84, 0.84 (s each, 3H each, Me × 5), 0.87 (d, *J* 6.8 Hz, 3H), 0.78 (d, *J* 11.5 Hz, 1H, H-5); ^{13}C NMR ($CDOD_3$): δ 175.0 (C-28), 139.6 (C-13), 126.9 (C-12), 107.1 (C-1′), 90.7 (C-3), 74.3, 72.8, 69.5, 66.4, 57.0, 54.4, 48.0, 42.2, 40.8, 40.4 (×2), 40.2, 39.9, 38.1, 37.8, 34.3, 31.8, 29.2, 28.6, 27.0, 25.3, 24.4, 24.1, 21.6, 19.3, 17.8, 17.7, 17.0, 16.1; ESI-MS (*m*/*z*): 611.0 $[M+Na]^+$ (Calcd 611.0).

3.4. Ursolic acid-3-yl 3,4-*O*-isopropylidine-α-L-arabinopyranoside (7)

To a solution of **6** (0.37 g, 0.63 mmol) and 2,2-dimethoxypropane (0.78 mL, 6.33 mmol) in dried DMF

(10 mL) was added TsOH (50 mg). After stirring at rt for 24 h, the mixture was neutralized with Et_3N and concentrated under vacuum. The residue was purified by silica gel column chromatography (2:1 petroleum ether–EtOAc) to give **7** as a white solid (0.37 g, 94%): R_f 0.30 (10:1 $CHCl_3$–MeOH); $[\alpha]_D^{20}$ +57.6 (*c* 0.17, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 11.25 (br s, 1H, –COO*H*), 5.23 (t, *J* 3.3 Hz, 1H, H-12), 4.21 (d, *J* 7.7 Hz, 1H, H-1′), 4.18–4.20 (m, 2H, H-4′, H-5′-1), 4.06 (dd, *J* 7.7, 5.9 Hz, 1H, H-3′), 3.76 (dd, *J* 13.9, 3.7 Hz, 1H, H-5′-2), 3.63 (t, *J* 7.7 Hz, 1H, H-2′), 3.12 (dd, *J* 4.4, 11.7 Hz, 1H, H-3), 2.18 (d, *J* 11.3 Hz, 1H, H-18), 1.54, 1.36 (s each, 3H each, Me_2C), 1.06, 0.99, 0.93, 0.81, 0.76 (s each, 3H each, Me × 5), 0.93 (d, *J* 8.0 Hz, 1H, H-30), 0.85 (d, *J* 6.6 Hz, 3H, H-29), 0.73 (d, *J* 11.3 Hz, 1H, H-5); ESI-MS (*m*/*z*): 651.1 $[M+Na]^+$ (Calcd 651.4).

3.5. 3-*O*-[2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)-3,4-*O*-isopropylidine-α-L-arabinopyranosyl]ursolic acid-28-*O*-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl] ester (9)

To a mixture of compound **7** (0.208 g, 0.33 mmol), **8** (0.736 g, 0.99 mmol), and powdered 4 Å molecular sieves in dried CH_2Cl_2 (10 mL) at 0 °C was added Me_3SiOTf (7.4 μL, 0.033 mmol). After the mixture was stirred at 0 °C for 1 h, the reaction was quenched with Et_3N. The solid was filtered off and the filtrate was then concentrated in vacuum. The resulting residue was purified by column chromatography (1:30 EtOAc–$CHCl_3$) to give compound **9** as a yellow solid (0.47 g, 80%); R_f 0.30 (1:20 EtOAc–$CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.26–8.06 (m, 40H, Ph × 8), 5.98 (t, *J* 9.5 Hz, 1H, H-3‴), 5.91 (t, *J* 9.9 Hz, 1H, H-3″), 5.88 (d, *J* 8.0 Hz, 1H, H-1‴), 5.68–5.75 (m, 3H, H-2‴, H-4‴, H-4″), 5.50 (dd, *J* 8.0, 9.5 Hz, 1H, H-2″), 5.32 (d, *J* 8.1 Hz, 1H, H-1″), 5.21 (t, *J* 3.3 Hz, 1H, H-12), 4.60 (dd, *J* 3.3, 12.1 Hz, 1H, H-6″-1), 4.54 (dd, *J* 2.9, 12.4 Hz, 1H, H-6‴-1), 4.50 (dd, *J* 4.7, 14.6 Hz, 1H, H-6″-2), 4.46 (dd, *J* 4.7, 12.1 Hz, 1H, H-6‴-2), 4.33 (d, *J* 6.6 Hz, 1H, H-1′), 4.23–4.26 (m, 1H, H-5‴), 4.10–4.15 (m, 2H, H-4′, H-5″), 3.87–3.94 (m, 3H, H-2′, H-3′, H-5′-1), 3.67 (dd, *J* 4.4, 12.8 Hz, 1H, H-5′-2), 2.94 (dd, *J* 4.4, 11.3 Hz, 1H, H-3), 2.12 (d, *J* 11.4 Hz, 1H, H-18), 1.49, 1.25 (s each, 3H each, –CMe_2), 0.96, 0.90, 0.87, 0 86, 0.40 (s each, 3H each, Me × 5), 0.81 (d, *J* 6.6 Hz, 3H, H-30), 0.70 (d, *J* 5.8 Hz, 3H, H-29), 0.49 (d, *J* 11.8 Hz, 1H, H-5).

3.6. 3-*O*-[2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)-α-L-arabinopyranosyl]ursolic acid-28-*O*-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl] ester (10)

A solution of **9** (0.470 g, 0.26 mmol) in 80% AcOH (15 mL) was stirred at 70 °C for 12 h and then concentrated in vacuum. The residue was directly purified by silica gel column chromatography (2:1→1:1 petroleum ether–EtOAc) to afford **10** (0.430 g, 94%) as a white solid: R_f 0.27 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +37.6 (*c* 0.12, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.26–8.03 (m, 40H, Ph × 8), 5.97 (t, *J* 10.1 Hz, 1H, H-3‴), 5.90 (dd, *J* 9.7, 12.8 Hz, 1H, H-3″), 5.88 (d, *J* 8.3 Hz, 1H, H-1‴), 5.67–5.75 (m, 3H, H-2‴, H-4‴, H-4″), 5.53 (dd, *J* 8.2, 9.6 Hz, 1H, H-2″), 5.22 (t, *J* 3.2 Hz, 1H, H-12), 5.11 (d, *J* 7.8 Hz, 1H, H-1″), 4.75 (d, *J* 2.8 Hz, 1H, H-1′), 4.59 (dd, *J* 3.2, 12.4 Hz, 1H, H-6″-1). 4.53 (dd, *J* 2.8, 9.1 Hz, 1H, H-6‴-1), 4.45–4.49 (m, 2H, H-6″-2, H-6‴-2), 4.23–4.26 (m, 1H, H-5‴), 4.16–4.19 (m, 1H, H-5″), 3.96 (t, *J* 3.7 Hz, 1H, H-2′), 3.68–3.72 (m, 2H, H-3′, H-4′), 3.63 (dd, *J* 8.7, 11.5 Hz, 1H, H-5′-1), 3.49 (dd, *J* 4.4, 11.5 Hz, 1H, H-5′-2), 3.02 (dd, *J* 4.6, 11.9 Hz, 1H, H-3), 2.95 (s, 1H, OH), 2.88 (s, 1H, OH), 2.13 (d, *J* 11.0 Hz, 1H, H-18), 0.89, 0.84, 0.73, 0.70, 0.44 (s each, 3H each, Me × 3), 0.82 (d, *J* 6.4 Hz, 3H), 0.48 (d, *J* 11.5 Hz, 1H, H-5); ^{13}C NMR ($CDCl_3$): δ 174.4 (C-28), 165.1, 165.0, 164.7, 164.6, 164.1 (×2), 163.7, 161.5, 136.3 (C-13), 127.3–132.5 (Ph–C), 126.6 (C-12), 100.5 (C-1′), 100.3 (C-1″), 90.9 (C-1‴), 88.9 (C-3), 76.0, 71.8, 71.7, 71.3, 70.9, 69.3, 69.1, 68.4, 68.2, 63.7, 62.0, 61.7, 54.0 (C-5), 51.4 (C-18), 47.1, 46.2, 40.8, 38.0, 37.9, 37.8, 37.7, 37.3, 35.4, 34.9, 30.9, 29.6, 29.4, 28.7, 26.9, 24.5, 22.8, 22.1, 20.1, 17.0, 16.0, 15.4, 14.3.

3.7. 3-*O*-[2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)-4-*O*-acetyl-α-L-arabinopyranosyl]ursolic acid-28-*O*-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl] ester (11)

Triethyl orthoacetate (0.48 mL, 2.4 mmol) and *p*-TsOH·H_2O (20 mg) were added to the solution of **10** (0.43 g, 0.24 mmol) in CH_2Cl_2 (10 mL). After the reaction mixture was stirred at rt overnight, 50% AcOH (10 mL) was added. The solution was vigorously stirred for 30 min, diluted with CH_2Cl_2 (100 mL), and successively washed with water (30 mL × 2), satd aq $NaHCO_3$ (30 mL × 2), and brine (30 mL × 2). The organic layer was dried over anhydrous Na_2SO_4 and then concentrated under vacuo. The residue was purified by silica gel column chromatography (2:1 petroleum ether–EtOAc) to give **11** (0.38 g, 86%) as a white solid: R_f 0.38 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +43.5 (*c* 0.17, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.26–7.98 (m, 40H, Ph × 8), 5.98 (t, *J* 9.6 Hz, 1H, H-3‴), 5.88–5.91 (m, 2H, H-1‴, H-3″), 5.71–5.76 (m, 3H, H-2‴, H-4‴, H-4″), 5.54 (dd, *J* 8.3, 10.1 Hz, 1H, H-2″), 5.23 (t, *J* 3.2 Hz, 1H, H-12), 5.20 (d, *J* 7.8 Hz, 1H, H-1″), 4.86–4.88 (m, 1H, H-4′), 4.60–4.62 (m, 2H, H-1′, H-6″-1), 4.45–4.56 (m, 3H, H-6″-2, H-6‴-1, H-6‴-2), 4.23–4.26 (m, 1H, H-5‴), 4.16–4.19 (m, 1H, H-5″), 3.94 (dd, *J* 5.9, 4.6 Hz, 1H, H-2′), 3.84–3.87 (m, 2H, H-3′, H-5′-1), 3.50 (dd, *J* 11.9, 3.2 Hz, 1H, H-5′-2), 3.02 (dd, *J* 4.6, 11.4 Hz, 1H, H-3), 2.14 (d, *J* 11.5 Hz, 1H, H-18),

1.96 (s, 3H, Ac), 0.91, 0.89, 0.73, 0.73, 0.43 (s each, 3H each, Me × 5), 0.81 (d, *J* 6.4 Hz, 3H, H-29), 0.50 (d, *J* 11.4 Hz, 1H, H-5); ^{13}C NMR ($CDCl_3$): δ 175.5 (C-28), 170.3, 166.2, 166.1, 165.8, 165.7, 165.2, 165.1 (×2), 164.8, 137.3 (C-13), 128.3–133.5 (Ph–C), 125.9 (C-12), 102.5 (C-1′), 101.2 (C-1″), 92.0 (C-1‴), 90.2 (C-3), 77.4 (C-2′), 72.8 (C-3″, C-3‴, C-5‴), 72.2 (C-2″, C-5″), 70.4 (C-2‴), 69.8 (C-3′), 69.6 (C-4″), 69.2 (C-4‴), 68.9 (C-4′), 63.1 (C-6″), 62.7 (C-6‴), 59.3 (C-5′), 55.2 (C-5), 52.5 (C-18), 48.1, 47.3, 41.8, 39.0, 38.9, 38.8, 38.4, 36.4, 35.9, 32.0, 30.5, 29.7, 28.2, 27.9, 25.7, 23.9, 23.2, 23.1, 21.1, 20.9, 18.0, 17.0, 16.4, 15.3.

3.8. 3-*O*-{[2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)]-[2,3,4-tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→3)]-4-*O*-acetyl-α-L-arabinopyranosyl}ursolic acid-28-*O*-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl] ester (12)

To a mixture of compound **11** (0.12 g, 0.067 mmol), benzoylated arabinopyranosyl donor **3** (0.16 g, 0.268 mmol), and powdered 4 Å molecular sieves in dried CH_2Cl_2 (5 mL) at −40 °C was added $BF_3{\cdot}OEt_2$ (8.5 μL, 0.067 mmol). The mixture was stirred at −40 °C for 12 h and the reaction was quenched with Et_3N. The solid was then filtered off and the filtrate concentrated in vacuo to give a yellow syrup, which was purified by column chromatography (4:1→2:1 petroleum ether–EtOAc) to give compound **12** as a white foam (0.07 g, 47%): R_f 0.17 (2:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +108.8 (*c* 0.17, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.26–8.27 (m, 55H, Ph × 11), 6.00 (t, *J* 9.6 Hz, 1H, H-3‴″), 5.88 (d, *J* 8.7 Hz, 1H, H-1‴″), 5.64–5.76 (m, 4H, H-2‴″, H-3″, H-4‴″, H-2‴), 5.40–5.47 (m, H-4″, H-3‴, H-2″), 5.35 (br s, 1H, H-4‴), 5.21–5.22 (m, 2H, H-4′, H-12), 4.71 (d, *J* 7.3 Hz, 1H, H-1″), 4.53–4.56 (m, 2H, H-1‴, H-6‴″-1), 4.48 (dd, *J* 11.9, 4.6 Hz, 1H, H-6‴″-2), 4.36 (dd, *J* 11.9, 3.7 Hz, 1H, H-6″-1), 4.24–4.28 (m, 2H, H-1′, H-5‴″), 4.19 (dd, *J* 11.9, 5.0 Hz, 1H, H-6″-2), 3.80–3.92 (m, 4H, H-2′, H-3′, H-5′-1, H-5‴-1), 3.45 (d, *J* 12.4 Hz, 1H, H-5′-2), 2.99 (dd, *J* 11.5, 4.1 Hz, 1H, H-3), 2.59 (m, 1H, H-5″), 2.40 (d, *J* 11.5 Hz, 1H, H-5‴-2), 2.22 (s, 3H, C*H*$_3$CO), 2.13 (d, *J* 11.5 Hz, 1H, H-18), 1.90 (td, *J* 9.7, 4.1 Hz, 1H, H-16-1), 1.77–1.79 (m, 3H), 1.10, 0.89, 0.69, 0.65, 0.41 (s each, 3H each, CH_3 × 5), 0.82 (d, *J* 6.4 Hz, 3H), 0.51 (d, *J* 13.3 Hz, 1H, H-5); ^{13}C NMR ($CDCl_3$): δ 175.4 (C-28), 170.5 (Me*C*O), 166.1, 165.9 (×2), 165.7 (×2), 165.6, 165.2, 165.1, 164.8, 164.7 (×2), 137.3 (C-13), 128.2–133.9 (Ph–C), 125.9 (C-12), 104.1 (C-1′), 100.4 (C-1″, C-1‴), 92.0 (C-1‴″), 90.4 (C-3), 76.6 (C-3′), 75.7 (C-2′), 69.3-72.8 (C-4′, C-2″, C-3″, C-4″, C-5″, C-2‴, C-3‴, C-2‴″, C-3‴″, C-4‴″, C-5‴″), 68.2 (C-4‴), 63.8 (C-5′), 63.4 (C-5‴), 63.1 (C-6″), 62.7 (C-6‴″), 55.5 (C-5), 52.5 (C-18), 48.1, 47.3, 41.8, 39.2, 39.0 (2 C), 38.7, 36.4, 35.9, 31.9, 30.5, 29.7, 28.3, 27.7, 25.8, 23.9, 23.2, 23.0, 22.7, 21.1, 18.0, 17.0, 16.4, 15.3.

3.9. Benzyl 2-*O*-levulinyl-3,4-*O*-isopropylidene-β-L-arabinopyranoside (15)

$BF_3{\cdot}Et_2O$ (0.75 mL) was added to the suspension of L-arabinose (5.0 g, 33.3 mmol) in BnOH (40 mL). The mixture was stirred at 90–100 °C for 2.5 h and the reaction was quenched with Et_3N. The mixture was poured into dry ether (250 mL), kept at 4 °C for 4 h, and then recrystallized from ether to give **13** (3.68 g, 46%). A solution of **13** (1.60 g, 6.66 mmol), 2,2-dimethoxypropane (1.65 mL, 13.32 mmol) and *p*-$TsOH{\cdot}H_2O$ (50 mg) in dried DMF (10 mL) was stirred at rt for 12 h. The mixture was neutralized with Et_3N, concentrated in vacuo and redissolved in EtOAc (100 mL). The solution was then washed with satd aq $NaHCO_3$ (30 mL × 2) and brine (30 mL × 2) successively. The organic layer was dried (Na_2SO_4) and concentrated to give a residue, which was purified by silica gel column chromatography (3:1 petroleum ether–EtOAc) to give **14** (0.74 g, 79%). To a solution of **14** (1.2 g, 4.28 mmol) in dried CH_2Cl_2 (15 mL) were added DCC (1.6 g, 7.70 mmol), DMAP (50 mg), and levulinic acid (1.5 g, 12.84 mmol). After stirring at rt for 12 h, the mixture was filtered and concentrated. The residue was purified by column chromatography (4:1 petroleum ether–EtOAc) to give **15** (1.62 g, 100%) as a white solid: R_f 0.50 (1:1 petroleum ether–EtOAc); ^{1}H NMR ($CDCl_3$): δ 7.26–7.33 (m, 5H, Ph), 5.00 (d, *J* 3.3 Hz, 1H, H-1), 4.92 (dd, *J* 8.0, 3.3 Hz, 1H, H-2), 4.72 (d, *J* 12.1 Hz, 1H, Ph–C*H*$_2$), 4.52 (d, *J* 12.1 Hz, 1H, Ph–C*H*$_2$–), 4.37 (dd, *J* 8.1, 5.5 Hz, 1H, H-3), 4.25–4.26 (dt, *J* 5.5, 1.8 Hz, 1H, H-4), 4.01–4.02 (m, 2H, H-5), 2.63–2.77 (m, 4H, Lev), 2.16 (s, 3H, Lev), 1.54, 1.36 (s each, 3H each, Me × 2).

3.10. Benzyl 2-*O*-levulinyl-4-*O*-acetyl-β-L-arabinopyranoside (17)

A suspension of **15** (1.62 g, 4.28 mmol) in 70% AcOH (30 mL) was stirred at 70 °C for 1 h and then concentrated and redissolved in CH_2Cl_2 (100 mL). The organic layer was successively washed with satd aq $NaHCO_3$ (30 mL × 2), and brine (30 mL × 2), dried over anhydrous Na_2SO_4, and then concentrated in vacuo. The residue was purified by column chromatography (50:1 $CHCl_3$–MeOH) to give a white solid **16** (1.34 g, 93%). A solution of **16** (1.34 g, 4.00 mmol), triethyl orthoacetate (2.02 mL, 10.0 mmol) and *p*-$TsOH{\cdot}H_2O$ (40 mg) in CH_2Cl_2 (25 mL) was stirred at rt for 1.5 h, 80% AcOH (10 mL) was added, and the mixture was vigorously stirred for another 30 min and then diluted with CH_2Cl_2 (70 mL). The solution was successively washed with water (30 mL × 2), satd aq $NaHCO_3$ (30 mL × 2), and brine (30 mL × 2), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (2:1 petroleum ether–EtOAc) to give **17** as a white solid (1.74 g, 94%):

R_f 0.20 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +194.7 (*c* 0.17, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.26–7.36 (m, 5H, Ph), 5.17–5.18 (m, 1H, H-4), 5.06–5.10 (m, 2H, H-1, H-3), 4.73 (d, *J* 11.9 Hz, 1H, PhCH_2–), 4.53 (d, *J* 11.9 Hz, 1H, PhCH_2–), 4.26 (dd, *J* 3.7, 9.6 Hz, 1H, H-2), 3.92 (dd, *J* 0.9, 13.3 Hz, 1H, H-5-1), 3.77 (dd, *J* 1.9, 12.8 Hz, 1H, H-5-2), 2.58–2.77 (m, 4H, Lev), 2.17, 2.16 (s each, 3H each, CH_3CO); ESI-MS (*m*/*z*): 402.8 $[M+Na]^+$ (Calcd 403.1).

3.11. Benzyl 2-*O*-levulinyl-3-*O*-(2,3,4-tri-*O*-benzoyl-α-L-arabinopyranosyl)-4-*O*-acetyl-α-L-arabinopyranoside (19)

To a solution of compound **17** (0.30 g, 0.79 mmol), benzoylated arabinopyranosyl donor **3** (0.72 g, 1.18 mmol), and powdered 4 Å molecular sieves in dried CH_2Cl_2 (10 mL) was added Me_3SiOTf (13.7 μL, 0.079 mmol). The mixture was stirred at −20 °C for 1 h, and the reaction was quenched with Et_3N. The solid was then filtered off and the filtrate concentrated under vacuum to give a yellow oil, which was purified by column chromatography (2:1 petroleum ether–EtOAc) to give compound **19** (0.57 g, 88%) as a white solid: R_f 0.35 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +194.3 (*c* 0.17, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.30–8.03 (m, 20H, Ph × 4), 5.66–5.68 (m, 1H, H-4′), 5.61–5.63 (m, 2H, H-2′, H-3′), 5.34 (m, 1H, H-4), 5.16 (dd, *J* 3.3, 10.3 Hz, 1H, H-2), 5.06 (d, *J* 3.7 Hz, 1H, H-1), 4.97 (d, *J* 5.2 Hz, 1H, H-1′), 4.48 (d, *J* 11.7 Hz, 1H, Ph–CH_2–), 4.69 (d, *J* 11.7 Hz, 1H, Ph–CH_2–), 4.29 (dd, *J* 3.7, 10.6 Hz, 1H, H-3), 4.23 (dd, *J* 5.5, 12.5 Hz, 1H, H-5′-1), 3.92 (dd, *J* 1.1, 13.2 Hz, 1H, H-5-1), 3.88 (dd, *J* 2.6, 12.4 Hz, 1H, H-5′-2), 3.73 (dd, *J* 2.2, 13.2 Hz, 1H, H-5-2), 2.25–2.54 (m, 4H, Lev), 2.07, 2.00 (s each, 3H each, Ac, Me); ^{13}C NMR ($CDCl_3$): δ 206.0, 171.9, 170.5, 165.6 (×2), 164.9, 128.0–137.0 (Ph–C), 100.9 (C-1′), 95.7 (C-1), 73.1 (C-3), 71.3 (C-4), 69.9–70.2 (C-2, C-2′, C-3′, Ph–*C*H_2–), 67.6 (C-4′), 61.2 (C-5′), 60.6 (C-5), 37.7, 29.7, 27.5, 21.0; ESI-MS (*m*/*z*): 846.8 $[M+Na]^+$ (Calcd 847.2).

3.12. Benzyl 2-*O*-levulinyl-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-4-*O*-acetyl-α-L-arabinopyranoside (18)

Compound **18** was synthesized from **17** by the same procedure as that used for compound **19** and was purified by column chromatography (2:1 petroleum ether–EtOAc) to give a white solid (79%): R_f 0.50 (1:1 petroleum ether–EtOAc). ^1H NMR ($CDCl_3$): δ 7.26–8.04 (m, 25H, Ph × 5), 5.88 (t, *J* 9.9 Hz, 1H, H-3′), 5.66 (t, 1H, *J* 9.9 Hz, 1H, H-4′), 5.48 (dd, *J* 7.7, 9.8 Hz, 1H, H-2′), 5.35–5.36 (m, 1H, H-4), 5.05 (dd, *J* 3.7, 10.2 Hz, 1H, H-2), 5.01–5.02 (m, 2H, H-1, H-1′), 4.63 (d, *J* 12.1 Hz, 1H, Ph–CH_2–), 4.58 (dd, *J* 3.3, 12.1 Hz, 1H, H-6′-1), 4.48 (dd, *J* 4.7, 12.1 Hz, 1H, H-6′-2), 4.43 (d, *J* 12.1 Hz, 1H, Ph–CH_2–), 4.21 (dd, *J* 3.7, 10.3 Hz, 1H, H-3), 4.14–4.22 (m, 1H, H-5′), 3.77 (d, *J* 13.2 Hz, 1H, H-5-1), 3.66 (dd, *J* 2.2, 13.2 Hz, 1H, H-5-2), 1.84–2.39 (m, 4H, Lev), 2.08, 2.05 (s each, 3H each, 2 × CH_3CO–); ^{13}C NMR ($CDCl_3$): δ 205.9, 171.7, 170.4, 166.0, 165.8, 165.1, 164.7, 128.0–137.0 (Ph–C), 101.6 (C-1′), 95.6 (C-1), 76.8, 73.7, 72.8, 72.0, 70.8, 70.0 (2C), 69.4, 62.8, 60.4, 37.6, 29.7, 27.2, 21.0.

3.13. 2-*O*-Levulinyl-3-*O*-(2,3,4-tri-*O*-benzoyl-α-L-arabinopyranosyl)-4-*O*-acetyl-β-L-arabinopyranosyl trichloroacetimidate (23)

A suspension of **19** (0.563 g, 0.682 mmol) and 10% Pd–C (0.2 g) in MeOH–CH_2Cl_2 (1:1, 12 mL) was stirred under H_2 atmosphere at rt for 14 h and then filtered. The filtrate was concentrated in vacuo to give a yellow syrup, which was purified by flash column chromatography (2:1 petroleum ether–EtOAc) to give **21** (0.440 g, 88%) as a white foam. The solution of **21** (0.440 g, 0.60 mmol), CCl_3CN (0.48 mL, 4.8 mmol), and DBU (44.8 μL, 0.3 mmol) in CH_2Cl_2 was stirred at rt for 2 h, then concentrated in vacuo. The resulting residue was purified by flash column chromatography (3:1 petroleum ether–EtOAc) to give **23** (0.30 g, 57%) as a white foam; R_f 0.50 (1:1 petroleum ether–EtOAc).

3.14. 2-*O*-Levulinyl-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-4-*O*-acetyl-β-L-arabinopyranosyl trichloroacetimidate (22)

Compound **20** was synthesized from **18** by the same procedure as that used for compound **21** and was purified by column chromatography (2:1 petroleum ether–EtOAc) to give **21** as white solid (81%): R_f 0.50 (1:2 petroleum ether–EtOAc). Compound **22** was synthesized from **20** by the same procedure as that used for compound **23**, purified by column chromatography (3:1 petroleum ether–EtOAc) to give **22** as a white solid (71%): R_f 0.50 (1:1 petroleum ether–EtOAc).

3.15. Ursolic acid-28-*O*-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl] ester (24)

Ursolic acid (0.20 g, 0.44 mmol) was dissolved in CH_2Cl_2 (20 mL) in the presence of K_2CO_3 (0.122 g, 0.88 mmol), Bu_4NBr (0.17 g, 0.528 mmol), and H_2O (1 mL). The vigorously stirred mixture was treated at reflux with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (0.22 g, 0.88 mmol) in several portions. After 8 h, when the reaction was complete, CH_2Cl_2 (70 mL) was added, and the solution was successively washed with satd aq $NaHCO_3$ (30 mL × 2), 5% $Na_2S_2O_3$ (30 mL × 2), and brine (30 mL × 2). The organic layer was then

dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography (3:1 petroleum ether–EtOAc) to give **24** as a white solid (0.34 g, 99%): R_f 0.24 (2:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +32.4 (*c* 0.17, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.56 (d, *J* 8.1 Hz, 1H, H-1′), 5.28 (t, *J* 3.3 Hz, 1H, H-12), 5.23 (t, *J* 9.5 Hz, 1H, H-3′), 5.15 (dd, *J* 8.4, 9.5 Hz, 1H, H-2′), 5.12 (t, *J* 9.9 Hz, 1H, H-4′), 4.27 (dd, *J* 4.4, 12.5 Hz, 1H, H-6′-1), 4.03 (dd, *J* 2.2, 12.5 Hz, 1H, H-6′-2), 3.77–3.80 (m, 1H, H-5′), 3.22 (dd, *J* 4.7, 11.3 Hz, 1H, H-3), 2.18 (d, *J* 11.4 Hz, 1H, H-18), 2.07, 2.03, 2.02, 2.01 (s each, 3H each, Ac × 4), 1.07, 0.98, 0.92, 0.78, 0.76 (s each, 3H each, Me × 5), 0.93 (d, *J* 5.8 Hz, 3H, H-30), 0.86 (d, *J* 8.2 Hz, 3H, H-29), 0.72 (d, *J* 11.0 Hz, 1H, H-5); ESI-MS (*m*/*z*): 808.9 $[M+Na]^+$ (Calcd 809.4).

3.16. 3-*O*-[2,3,4-Tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→3)-2-*O*-levulinyl-4-*O*-acetyl-α-L-arabinopyranosyl]ursolic acid-28-*O*-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl] ester (25)

To a mixture of **24** (0.18 g, 0.23 mmol), **23** (0.30 g, 0.34 mmol), and powdered 4 Å molecular sieves in dried CH_2Cl_2 (10 mL) was added Me_3SiOTf (7.9 μL, 0.045 mmol) at −20 °C under Ar protection. The mixture was stirred under these conditions for 1 h, then neutralized with Et_3N. The solid was then filtered off and the filtrate was concentrated under vacuum to give a yellow syrup, which was purified by column chromatography (2:1 petroleum ether–EtOAc) to give compound **25** (0.30 g, 88%) as a white solid; R_f 0.50 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +72.9 (*c* 0.17, $CHCl_3$); ^1H NMR (DMSO): δ 7.36–7.96 (m, 15H, Ph × 3), 5.78 (d, *J* 8.0 Hz, 1H, H-1‴), 5.71 (dd, *J* 3.7, 9.5 Hz, 1H, H-3″), 5.60–5.61 (m, 1H, H-4″), 5.42 (t, *J* 9.5 Hz, 1H, H-3‴), 5.40 (dd, *J* 7.0, 9.5 Hz, 1H, H-2″), 5.19–5.20 (m, 1H, H-4′), 5.16 (t, *J* 3.3 Hz, 1H, H-12), 5.08 (d, *J* 7.0 Hz, 1H, H-1″), 4.91–4.95 (m, 2H, H-2‴, H-4‴), 4.88 (dd, *J* 7.7, 9.5 Hz, 1H, H-2′), 4.43 (d, *J* 7.7 Hz, 1H, H-1′), 4.12-4.17 (m, 3H, H-5‴, H-3′, H-6‴-1), 4.08 (dd, *J* 2.2, 13.6 Hz, 1H, H-5″-1), 4.05 (d, *J* 11.7 Hz, 1H, H-5″-2), 3.91 (d, *J* 9.7 Hz, 1H, H-6‴-2), 3.78 (d, *J* 11.7 Hz, 1H, H-5′-1), 3.67 (d, *J* 12.5 Hz, 1H, H-5′-2), 3.01 (dd, *J* 4.4, 12.1 Hz, 1H, H-3), 2.08–2.41 (m, 4H, Lev), 2.07 (d, *J* 11.3 Hz, 1H, H-18), 2.04, 2.02, 1.99, 1.98, 1.97, 1.95 (s each, 3H, Ac × 5, $CH_3COCH_2CH_2COO$), 1.02, 0.82, 0.79, 0.56 (s each, 3H, Me × 4), 0.89 (d-like, 3H, H-30), 0.80 (d, *J* 6.2 Hz, 1H, H-29), 0.68 (br s, 4H, Me, H-5); ^{13}C NMR ($CDCl_3$): δ 206.5, 175.3 (C-28), 171.1, 170.6 (×2), 170.1, 169.4, 169.0, 165.6 (×2), 165.0, 137.2 (C-13), 126.2–133.4 (Ph–C), 126.1 (C-12), 103.3 (C-1′), 100.2 (C-1″), 91.6 (C-1‴), 89.9 (C-3), 77.0 (C-3′), 72.9 (C-3‴), 72.4 (C-5‴), 71.2, 70.2 (C-2″), 69.9 (C-2‴), 69.2 (C-3″), 68.0 (C-4‴), 67.2 (C-4″), 64.0 (C-5′), 61.6 (C-6‴), 60.4 (C-5″), 55.5 (C-5), 52.6 (C-18), 48.1, 47.5, 42.0, 39.5, 39.0, 38.9, 38.8, 38.6, 37.8, 36.6, 35.9, 33.2, 30.5, 29.8 (×2), 25.8, 24.0, 23.3, 21.1, 20.6, 18.1, 17.0 (×2), 16.4, 15.4.

3.17. 3-*O*-[2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-levulinyl-4-*O*-acetyl-α-L-arabinopyranosyl]ursolic acid-28-*O*-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl] ester (26)

Compound **26** was synthesized from **24** by the same procedure as that used for compound **25**, and was purified by column chromatography (2:1 petroleum ether–EtOAc) giving **26** as a white solid (96%): R_f 0.30 (1:2 petroleum ether–EtOAc); ^1H NMR ($CDCl_3$): δ 7.27–8.05 (m, 20H, Ph × 4), 5.95 (t, *J* 9.5 Hz, 1H, H-3″), 5.67 (t, *J* 9.9 Hz, 1H, H-4″), 5.54 (d, *J* 8.0 Hz, 1H, H-1‴), 5.45 (dd, *J* 8.0, 9.9 Hz, 1H, H-2″), 5.26–5.27 (m, 2H, H-12, H-4′), 5.23 (t, *J* 9.5 Hz, 1H, H-3‴), 5.15–5.18 (m, 2H, H-2′, H-2‴), 5.11 (t, *J* 9.9 Hz, 1H, H-4‴), 5.06 (d, *J* 7.7 Hz, 1H, H-1″), 4.60 (dd, *J* 3.3, 12.1 Hz, 1H, H-6″-1), 4.51 (dd, *J* 4.8, 12.1 Hz, 1H, H-6″-2), 4.27 (dd, *J* 4.4, 12.1 Hz, 1H, H-6‴-1), 4.25 (d, *J* 7.7 Hz, 1H, H-1′), 4.19–4.21 (m, 1H, H-5″), 4.02 (dd, *J* 1.9, 12.1 Hz, 1H, H-6‴-2), 3.95 (dd, *J* 2.2, 13.6 Hz, 1H, H-5′-1), 3.89 (dd, *J* 3.7, 9.9 Hz, 1H, H-3′), 3.76-3.78 (m, 1H, H-5‴), 3.37 (d, *J* 12.4 Hz, 1H, H-5′-2), 2.98 (dd, *J* 4.4, 11.4 Hz, 1H, H-3), 2.16–2.43 (m, 4H, $CH_3CH_2CH_2CO_2$), 2.17 (d, *J* 12.1 Hz, 1H, H-18), 2.10, 2.06, 2.05, 2.02, 2.01, 2.01 (s each, 3H each, Ac × 5), 1.03, 0.86, 0.82, 0.73, 0.65 (s each, 3H each, CH_3 × 5), 0.93 (d, *J* 5.9 Hz, 3H, H-30), 0.85 (d, *J* 6.6 Hz, 3H, H-29), 0.64 (d, *J* 7.3 Hz, 1H, H-5); ^{13}C NMR ($CDCl_3$): δ 206.4, 175.3 (C-28), 171.2, 170.8, 170.6, 170.1, 169.5, 169.0, 166.0, 165.8, 165.1, 164.8, 137.1 (C-13), 128.3–133.4 (Ph–C), 126.1 (C-12), 103.4 (C-1′), 100.9 (C-1″), 91.5 (C-1‴), 89.7 (C-3), 76.6 (C-3′), 72.8 (C-3″), 72.7 (C-5‴), 72.4 (C-3‴), 72.2 (C-5″), 72.0 (C-2″), 71.4 (C-2‴), 69.9 (C-4′, C-4″), 69.6 (C-2′), 68.0 (C-4‴), 63.8 (C-5′), 62.9 (C-6″), 61.5 (C-6‴), 55.5 (C-5), 52.5 (C-18), 48.1, 47.5, 42.0, 39.5, 39.0, 38.8 (2C), 38.6, 37.6, 36.6, 35.9, 33.2, 30.5, 29.8, 29.7, 28.1, 27.8, 27.6, 25.8, 24.0, 23.2, 21.1, 21.0, 20.6 (2C), 18.1, 17.0, 16.9, 16.3, 15.4, 14.2.

3.18. 3-*O*-[2,3,4-Tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→3)-4-*O*-acetyl-α-L-arabinopyranosyl]ursolic acid-28-*O*-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl] ester (27)

To a solution of **25** (0.30 g, 0.20 mmol) in CH_2Cl_2–MeOH (1:1, 10 mL) was added $NH_2NH_2{\cdot}HOAc$ (0.061 g, 0.66 mmol). After being stirred at rt for 3 h, the mixture was concentrated in vacuum to give a yellow syrup, which was purified by column chromatography (2:1 petroleum ether–EtOAc) to give compound **27** (0.256 g, 91%) as a white solid: R_f 0.48 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +85.9 (*c* 0.17, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.33–8.05 (m, 15H, Ph × 3), 5.66–5.68 (m,

2H, H-2″, H-4″), 5.59 (dd, *J* 3.7, 8.4 Hz, 1H, H-3″), 5.54 (d, *J* 8.0 Hz, 1H, H-1‴), 5.27 (t, *J* 3.7 Hz, 1H, H-12), 5.23 (t, *J* 9.2 Hz, 1H, H-3‴), 5.15–5.20 (m, 3H, H-2‴, H-1″, H-4′), 5.12 (t, *J* 9.9 Hz, 1H, H-4‴), 4.25–4.28 (m, 2H, H-5″-1, H-6‴-1), 4.21 (d, *J* 7.3 Hz, 1H, H-1′), 4.03 (dd, *J* 2.2, 12.4 Hz, 1H, H-6‴-2), 3.98 (dd, *J* 1.9, 13.6 Hz, 1H, H-5′-1), 3.89 (dd, *J* 2.6, 12.8 Hz, 1H, H-5″-2), 3.82 (dd, *J* 3.3, 9.9 Hz, 1H, H-3′), 3.76–3.79 (m, 2H, H-5‴, H-2′), 3.51 (dd, *J* 12.5 Hz, 1H, H-5′-2), 3.12 (dd, *J* 4.4, 11.8 Hz, 1H, H-3), 2.18 (d, *J* 11.0 Hz, 1H, H-18), 2.06, 2.02, 2.02, 2.01, 1.96 (s each, 3H each, 5 × Ac), 1.05, 0.98, 0.91, 0.80, 0.75 (s each, 3H each, 5 × Me), 0.93 (d, *J* 5.8 Hz, 3H, H-30), 0.85 (d, *J* 6.2 Hz, 3H, H-29), 0.71 (d, *J* 11.8 Hz, 1H, H-5). ESI-MS (*m*/*z*): 1427.9 $[M+Na]^+$ (Calcd 1427.6).

3.19. 3-*O*-[2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-4-*O*-acetyl-α-L-arabinopyranosyl]ursolic acid-28-*O*-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl] ester (28)

Compound **28** was synthesized from **26** by the same procedure as that used for compound **27**, and it was purified by column chromatography (2:1 petroleum ether–EtOAc) giving **28** as a white solid (90%): R_f 0.30 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +40.0 (*c* 0.17, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.27–8.03 (m, 20H, Ph × 4), 5.88 (t, *J* 9.9 Hz, 1H, H-3″), 5.68 (t, *J* 9.5 Hz, 1H, H-4″), 5.54 (d, *J* 8.0 Hz, 1H, H-1‴), 5.51 (dd, *J* 8.0, 9.9 Hz, 1H, H-2″), 5.28 (t, *J* 3.3 Hz, 1H, H-12), 5.22–5.25 (m, 2H), 5.17–5.19 (m, 2H), 5.12 (t, *J* 9.9 Hz, 1H), 4.60 (dd, *J* 3.3, 12.1 Hz, 1H, H-6″-1), 4.51 (dd, *J* 5.1, 12.1 Hz, 1H, H-6″-2), 4.27 (dd, *J* 4.4, 12.5 Hz, 1H, H-6‴-1), 4.11–4.14 (m, 2H), 4.03 (dd, *J* 2.2, 12.5 Hz, 1H, H-6‴-2), 3.92 (d, *J* 11.7 Hz, 1H, H-5′-1), 3.78 (dd, *J* 3.3, 9.1 Hz, 1H), 3.70 (dd, *J* 7.7, 9.5 Hz, 1H), 3.40 (d, *J* 12.8 Hz, 1H, H-5′-2), 3.08 (dd, *J* 4.4, 11.3 Hz, 1H, H-3), 2.18 (d, *J* 10.3 Hz, 1H, H-18), 2.06 (s, 3H, CH_3CO), 2.01–2.03 (m, 12H, Ac × 4), 1.05, 0.96, 0.89, 0.78, 0.74 (s each, 3H each, CH_3 × 5), 0.93 (d, *J* 6.2 Hz, 3H), 0.85 (d, *J* 6.2 Hz, 3H), 0.70 (d, *J* 12.1 Hz, 1H, H-5); ESI-MS (*m*/*z*): 1561.9 $[M+Na]^+$ (Calcd 1561.6).

3.20. 3-*O*-{[2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1→2)]-[2,3,4-tri-*O*-benzoyl-α-L-arabinopyranosyl-(1→3)]-4-*O*-acetyl-α-L-arabinopyranosyl}ursolic acid-28-*O*-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl] ester (29)

To a mixture of compound **27** (80.0 mg, 0.057 mmol) and powdered 4 Å molecular sieves in dried CH_2Cl_2 (5 mL) was added Me_3SiOTf (1.0 μL, 5.7 μmol) at −40 °C. To the mixture stirred for 30 min was added acetylated glucopyranosyl donor **32** (168.8 mg, 0.342 mmol). The reaction continued for 12 h, and then was quenched with Et_3N. The solid was filtered off and the filtrate was concentrated under vacuum to give a yellow syrup, which was purified by column chromatography (2:1→1:1 petroleum ether–EtOAc) to give compound **29** (52.8 mg, 53%) as a white solid: R_f 0.30 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +37.9 (*c* 0.17, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.10–8.09 (m, 15H, Ph × 3), 5.69–5.71 (m, 1H, H-4‴), 5.64–5.66 (m, 2H, H-2‴, H-3‴), 5.54 (d, *J* 8.0 Hz, 1H, H-1⁗), 5.27 (t, *J* 3.3 Hz, 1H, H-12), 5.24 (t, *J* 9.1 Hz, 1H, H-3⁗), 5.19 (br s, 1H, H-4′), 5.17 (dd, *J* 8.5, 9.5 Hz, 1H, H-2⁗), 5.12 (t, *J* 9.5 Hz, 1H, H-4⁗), 5.08 (t, *J* 9.5 Hz, 1H, H-3″), 5.02 (d, *J* 3.7 Hz, 1H, H-1‴), 4.96 (t, *J* 9.5 Hz, 1H, H-4″), 4.93 (dd, *J* 8.0, 9.9 Hz, 1H, H-2″), 4.68 (d, *J* 8.0 Hz, 1H, H-1″), 4.26–4.34 (m, 3H, H-1′, H-5‴-1, H-6⁗-1), 4.11 (dd, *J* 4.7, 11.7 Hz, 1H, H-6″-1), 4.04 (dd, *J* 2.2, 12.4 Hz, 1H, H-6⁗-2), 3.96–4.01 (m, 3H, H-2′, H-3′, H-5′-1), 3.89 (d, *J* 12.8 Hz, 1H, H-5‴-2), 3.85 (dd, *J* 3.7, 12.1 Hz, 1H, H-6″-2), 3.77–3.79 (m, 1H, H-5⁗), 3.45 (d, *J* 11.8 Hz, 1H, H-5′-2), 3.00 (dd, *J* 4.7, 11.3 Hz, 1H, H-3), 2.90–2.98 (m, 1H, H-5″), 2.17 (d, *J* 11.3 Hz, 1H, H-18), 2.07, 2.05, 2.04, 2.02 (×3), 2.00, 1.98, 1.94 (s each, 27H, Ac × 9), 1.06, 1.04, 0.87, 0.78, 0.74 (s each, 3H each, Me × 5), 0.93 (d, *J* 5.8 Hz, 3H), 0.85 (d, *J* 6.2 Hz, 3H), 0.67 (d, *J* 11.3 Hz, 1H, H-5); ^{13}C NMR ($CDCl_3$): δ 175.4 (C-28), 170.7, 170.6, 170.4, 170.1 (×2), 169.5, 169.4, 169.2, 169.0, 165.5, 165.4, 164.6, 137.2 (C-13), 126.9–133.8 (Ph–C), 126.1 (C-12), 103.8 (C-1′), 99.7 (C-1″), 99.4 (C-1‴), 91.6 (C-1⁗), 90.3 (C-1), 74.6, 73.0, 72.8, 72.4, 71.7, 71.2, 69.9, 69.2, 68.1, 68.0, 66.9, 61.5, 61.4, 60.4, 55.5 (C-5), 52.6 (C-18), 48.1, 47.5, 42.0, 39.5, 39.1, 39.0, 38.8, 38.6, 36.6, 35.9, 33.2, 30.5, 28.4, 28.1, 27.8, 25.8, 24.0, 23.3, 20.6–21.1 (Ac × 9), 18.1, 17.0 (2C), 16.4, 15.8, 15.6; ESI-MS (*m*/*z*): 1757.9 $[M+Na]^+$ (Calcd 1757.7).

3.21. 3-*O*-{[2,3,4-Tetra-*O*-acetyl-β-D-xylopyranosyl-(1→2)]-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)]-4-*O*-acetyl-α-L-arabinopyranosyl}ursolic acid-28-*O*-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl] ester (30)

Compound **30** was synthesized from **28** by the same procedure as that used for compound **29**, and was purified by column chromatography (2:1→1:1 petroleum ether–EtOAc) giving **20** as a white solid (97%): R_f 0.30 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +22.9 (*c* 0.17, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.10–8.04 (m, 20H, Ph × 4), 5.87 (t, *J* 9.6 Hz, 1H, H-3‴), 5.67 (t, *J* 9.6 Hz, 1H, H-4‴), 5.54 (d, *J* 8.3 Hz, 1H, H-1⁗), 5.52 (t, *J* 8.7 Hz, 1H, H-2‴), 5.27 (t, *J* 3.2 Hz, 1H, H-12), 5.25 (t, *J* 9.6 Hz, 1H, H-3⁗), 5.20 (br s, 1H, H-4′), 5.17 (dd, *J* 8.2, 9.6 Hz, 1H, H-2⁗), 5.11 (t, *J* 10.1 Hz, 1H, H-4⁗), 5.00 (d, *J* 7.3 Hz, 1H, H-1‴), 4.80–4.81 (m, 2H, H-2″, H-3″), 4.70–4.73 (m, 1H, H-4″), 4.58 (dd, *J* 3.7, 8.7 Hz, 1H, H-6‴-1), 4.54 (dd, *J* 5.5, 12.4 Hz, 1H, H-6‴-2), 4.42 (d, *J* 7.3 Hz, 1H, H-1″), 4.27 (dd, *J* 4.6, 12.4 Hz, 1H, H-6⁗-1), 4.18 (d, *J* 7.3 Hz, 1H, H-1′), 4.04–4.06 (m, 1H, H-5‴), 4.02 (dd, *J* 1.8, 10.1 Hz, 1H, H-6⁗-2), 3.86–

3.92 (m, 2H, H-2′, H-5′-1), 3.81 (dd, *J* 3.7, 9.7 Hz, 1H, H-3′), 3.78–3.80 (m, 1H, H-5‴′), 3.71 (dd, *J* 5.5, 11.5 Hz, 1H, H-5″-1), 3.27 (d, *J* 12.4 Hz, 1H, H-5′-2), 2.99 (d, *J* 4.6, 11.5 Hz, 1H, H-3), 2.32 (d, *J* 9.6 Hz, 1H, H-5″-2), 2.17 (d, *J* 10.3 Hz, 1H, H-18), 2.16, 2.14, 2.06, 2.04, 2.02 (×2), 2.00 (s each, 24H, Ac × 8), 1.05, 0.97, 0.88, 0.78, 0.74 (s each, 3H each, Me × 5), 0.90 (d, *J* 6.4 Hz, 3H, H-30), 0.85 (d, *J* 6.4 Hz, 3H, H-29), 0.66 (d, *J* 11.9 Hz, 1H, H-5); ^{13}C NMR ($CDCl_3$): δ 175.4 (C-28), 170.6, 170.5, 170.1, 170.0, 169.6, 169.5, 169.3, 169.0, 166.0, 165.7, 165.1, 164.7, 137.2 (C-13), 127.7–133.5 (Ph–C), 126.2 (C-12), 104.1 (C-1′), 100.9 (C-1‴), 99.8 (C-1″), 91.6 (C-1‴′), 90.0 (C-3), 78.2, 74.7, 72.9, 72.6, 72.4, 72.3, 72.2, 70.4, 69.9, 69.7, 68.8, 68.0, 62.9, 61.6 (2C), 55.6 (C-5), 52.6 (C-18), 48.1, 47.5, 42.0, 39.5, 39.0, 38.8, 38.7, 36.6, 35.9, 32.2, 30.5, 28.4, 28.1, 27.6, 26.0, 24.0, 23.3, 20.6–21.1 (Ac × 8), 18.1, 17.0, 16.9, 15.5; ESI-MS (*m*/*z*): 1819.9 $[M+Na]^+$ (Calcd 1819.7).

3.22. 3-*O*-{[β-D-Glucopyranosyl-(1→2)]-[α-L-arabinopyranosyl-(1→3)]-α-L-arabinopyranosyl}ursolic acid-28-*O*-[β-D-glucopyranosyl] ester (1)

Compound **12** (0.079 g, 0.036 mmol) was dissolved in MeOH–CH_2Cl_2 (2:1, 6 mL), and then NaOMe in MeOH (20 mg, 50%) was added. After stirring at rt for 4 h, the solution was neutralized with ion-exchange resin (H^+), and then filtered and concentrated. The residue was purified by column chromatography (20:1→2:1 $CHCl_3$–MeOH) to afford **1** as an amorphous solid (0.037 g, 99%): Compound **1** was also obtained from **29** by the same treatment for **12**; R_f 0.25 (2:1:0.1 $CHCl_3$–MeOH–H_2O); $[\alpha]_D^{20}$ +29.7 (*c* 0.17, CH_3OH); ^{1}H NMR (CD_3OD): δ 5.33 (d, *J* 8.2 Hz, 1H, H-1‴′), 5.23 (t, *J* 3.7 Hz, 1H, H-12), 4.83 (d, *J* 7.7 Hz, 1H, H-1″), 4.51 (d, *J* 7.3 Hz, 1H, H-1‴), 4.40 (d, *J* 7.7 Hz, 1H, H-1′), 4.00 (br s, 1H, H-4′), 3.97 (dd, *J* 7.8, 9.2 Hz, 1H, H-2′), 3.76–3.86 (m, 7H), 3.66–3.69 (m, 1H), 3.64 (dd, *J* 7.3, 9.1 Hz, 1H, H-2‴), 3.52–3.56 (m, 3H), 3.49 (dd, *J* 3.2, 9.2 Hz, 1H, H-3‴) 3.26–3.41 (m, 4H), 3.17 (dd, *J* 4.6, 11.9 Hz, 1H, H-3), 3.10 (dd, *J* 7.8, 9.2 Hz, 1H, H-2″), 3.05 (t, *J* 9.2 Hz, 1H, H-4″), 2.22 (d, *J* 11.5 Hz, 1H, H-18), 1.32–1.40 (m, 7H), 1.10, 1.06, 0.96, 0.85, 0.82 (s each, 3H each, CH_3 × 5), 0.88 (d, *J* 6.4 Hz, 3H), 0.75 (d, *J* 11.5 Hz, 1H, H-5); ^{13}C NMR (CD_3OD): δ 177.9 (C-28), 139.1 (C-13), 127.2 (C-12), 106.1 (C-1′), 105.8 (C-1‴), 103.6 (C-1″), 95.7 (C-1‴′), 91.9 (C-3), 84.1 (C-3′), 78.6, 78.4, 78.3 ,78.2, 76.5 (C-2′), 76.1 (C-2″), 74.4 (C-3‴), 73.9 (C-2‴′), 72.8 (C-2‴), 72.5, 71.2, 70.0 (C-4′), 69.9 (C-4‴), 67.2 (C-5′), 66.6, 63.7, 62.5, 57.0, 54.8, 54.2, 43.3, 41.0, 40.6, 40.3, 40.1, 37.8, 37.5, 34.3, 31.7, 29.3, 28.3, 27.2, 25.2, 24.4, 24.0, 21.5, 19.3, 17.9, 16.9, 16.1; ESI-MS (*m*/*z*): 1067.5420 $[M+Na]^+$ (Calcd 1067.5403).

3.23. 3-*O*-{[β-D-Xylopyranosyl-(1→2)]-[β-D-glucopyranosyl-(1→3)]-α-L-arabinopyranosyl}ursolic acid-28-*O*-[β-D-glucopyranosyl] ester (2)

Compound **30** (0.079 g, 0.036 mmol) was dissolved in MeOH–CH_2Cl_2 (2:1, 6 mL), and then NaOMe in MeOH (20 mg, 50%) was added. After stirring at rt for 4 h, the solution was neutralized with ion-exchange resin (H^+), and then filtered and concentrated. The residue was purified by column chromatography (20:1→2:1 $CHCl_3$–MeOH) to afford **2** as an amorphous solid (0.037 g, 98%): R_f 0.30 (2:1:0.1 $CHCl_3$–MeOH–H_2O); $[\alpha]_D^{20}$ +22.6 (*c* 1.15, CH_3OH); ^{1}H NMR (Pyridine-d_5): δ 6.28 (d, *J* 8.0 Hz, 1H, H-1‴′), 5.43 (t-like, 1H, H-12), 5.40 (d, *J* 7.7 Hz, 1H, H-1″), 5.31 (d, *J* 7.7 Hz, 1H, H-1‴), 4.74 (d, *J* 7.0 Hz, 1H, H-1′), 4.67 (dd, *J* 7.0, 9.2 Hz, 1H, H-2′), 4.00-4.49 (m, 16H), 3.63 (br d, *J* 11.7 Hz, 1H), 3.25 (dd, *J* 4.0, 11.8 Hz, 1H, H-3), 2.51 (d, *J* 11.3 Hz, 1H, H-18), 1.28, 1.19, 1.13, 1.09, 0.86 (s each, 3H each, Me × 5), 0.92 (d, *J* 6.0 Hz, 3H, H-30), 0.88 (d-like, 3H, H-29), 0.76 (d, *J* 12.1 Hz, 1H, H-5); ^{13}C NMR (Pyridine-d_5): δ 176.2 (C-28), 138.4 (C-13), 126.1 (C-12), 105.7 (C-1′), 105.1 (C-1″, C-1‴), 95.7 (C-1‴′), 89.2 (C-3), 83.7 (C-3′), 79.2 (C-3‴′), 79.1 (C-5‴′), 78.9 (C-3‴), 78.5 (C-3″), 78.4 (C-5‴), 77.4 (C-2′), 76.0 (C-2″), 75.3 (C-2‴), 74.1 (C-2‴′), 71.5 (C-4″), 71.3 (C-4‴), 71.1 (C-4‴′), 69.0 (C-4′), 67.1 (C-5″), 66.2 (C-5′), 62.5 (C-6‴), 62.2 (C-6‴′), 56.0 (C-5), 53.3 (C-18), 48.3 (C-17), 48.0 (C-9), 42.5 (C-14), 40.1 (C-8), 39.8 (C-20), 39.3 (C-19), 39.1 (C-4), 38.9 (C-1), 36.9 (C-10), 36.8 (C-22), 33.5 (C-7), 30.8 (C-21), 28.6 (C-15), 27.8 (C-23), 26.7 (C-2), 24.6 (C-16), 23.8 (C-27), 23.6 (C-11), 21.3 (C-30), 18.5 (C-6), 17.6 (C-29), 17.4 (C-26), 16.5 (C-25), 15.7 (C-24); ESI-MS (*m*/*z*): 1067.5405 $[M+Na]^+$ (Calcd 1067.5403).

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