Triterpene Glycosides from the Stems of *Akebia quinata*

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The stems of *Akebia quinata* have been analyzed for their triterpene glycoside constituents, resulting in the isolation of six new triterpene glycosides, along with 19 known ones. On the basis of extensive spectroscopic analysis, including 2D NMR data, and chemical evidence, the structures of the new compounds were determined to be 3β-[(*O*-β-D-glucuronopyranosyl-(1→3)-α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester, 3β-[(*O*-β-D-glucuronopyranosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester, 3β-[(*O*-β-D-glucuronopyranosyl-(1→3)-α-L-arabinopyranosyl)oxy]-23-hydroxyolean-12-en-28-oic acid *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester, 3β-[(*O*-β-D-glucuronopyranosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl)oxy]-23-hydroxyolean-12-en-28-oic acid *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester, 3β-[(*O*-β-D-glucopyranosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl)oxy]-29-hydroxyolean-12-en-28-oic acid, and 3β-[(*O*-β-D-glucopyranosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl)oxy]-23,29-dihydroxyolean-12-en-28-oic acid, respectively. The main triterpene glycosides contained in the stems of *A. quinata* were found to have two sugar units at C-3 and C-28 of the aglycone in this study, whereas those of *Akebia trifoliate* were reported to possess one sugar unit at C-28 of the aglycone. It may be possible to distinguish between *A. quinata* and *A. trifoliate* chemically by comparing their triterpene glycoside constituents.

Key words Akebia Stem; *Akebia quinata*; *Akebia trifoliate*; Lardizabalaceae; stem; triterpene glycoside

Akebia Stem is a crude drug mainly used in Kampo prescriptions for its diuretic and antiphlogistic effects. According to the *Pharmacopoeia of Japan* (XV), Akebia Stem is prepared from the stems of *Akebia quinata* (HOUTT.) DECNE or *Akebia trifoliate* (THUNB.) KOIDZ. (Lardizabalaceae). Previously, we performed a systematic phytochemical examination of *A. trifoliate* stems and isolated a total of 25 triterpene and triterpene glycosides, some of which were new compounds.[1] In a continuous study of the original plants of Akebia Stem, a phytochemical analysis was carried out on the stems of *A. quinata* with particular attention paid to the triterpene glycoside constituents, resulting in the isolation of six new triterpene glycosides, along with 19 known ones. The structural determination of the new compounds on the basis of extensive spectroscopic analysis, including 2D NMR data, and chemical evidence, is mainly described in this paper.

Results and Discussion

The stems of *A. quinata* were extracted with hot MeOH. The concentrated MeOH extract was passed through a porous-polymer polystyrene resin (Diaion HP-20) column, eluted with 30% MeOH, EtOH, and EtOAc. The EtOH eluate fraction, in which triterpene glycosides were enriched, was subjected to a series of chromatographic separations, resulting in the isolation of compounds **1** (4.5 mg), **2** (15.3 mg), **3** (11.9 mg), **4** (12.3 mg), **5** (22.3 mg), **6** (20.4 mg), **7** (123 mg), **8** (1.51 g), **9** (278 mg), **10** (126 mg), **11** (32.6 mg), **12** (3.11 g), **13** (44.8 mg), **14** (26.8 mg), **15** (20.6 mg), **16** (27.6 mg), **17** (146 mg), **18** (1.58 g), **19** (919 mg), **20** (112 mg), **21** (97.3 mg), **22** (119 mg), **23** (94.0 mg), **24** (10.8 mg), and **25** (25.7 mg). The structures of the known compounds were identified as 3β-[(α-L-arabinopyranosyl)-oxy]olean-12-en-28-oic acid (**1**),[2] 3β-[(*O*-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid (**2**),[3] 3β-[(*O*-β-D-glucopyranosyl-(1→3)-α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid (**3**),[4] 3β-[(*O*-β-D-glucopyranosyl-(1→2)-*O*-[β-D-glucopyranosyl-(1→3)]-α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid (**4**),[5] 3β-[(*O*-β-D-glucopyranosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid (**5**),[6] 3β-[(*O*-β-D-glucuronopyranosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid (**6**),[1] 3β-[α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester (**7**),[7] 3β-[(*O*-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester (**8**),[1] 3β-[(*O*-β-D-glucopyranosyl-(1→3)-α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester (**9**),[8] 3β-[(*O*-β-D-glucopyranosyl-(1→2)-*O*-[β-D-glucopyranosyl-(1→3)]-α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester (**11**),[9] 3β-[(*O*-β-D-glucopyranosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester (**12**),[10] 3β-[(α-L-arabinopyranosyl)oxy]-23-hydroxyolean-12-en-28-oic acid (**14**),[2] 23-hydroxy-3β-[(*O*-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid (**15**),[2] 3β-[(*O*-β-D-glucopyranosyl-(1→3)-α-L-arabinopyranosyl)oxy]-23-hydroxyolean-12-en-28-oic acid (**16**),[11] 3β-[(*O*-β-D-glucopyranosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl)oxy]-23-hydroxyolean-12-en-28-oic acid (**17**),[10] 23-hydroxy-3β-[(*O*-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-

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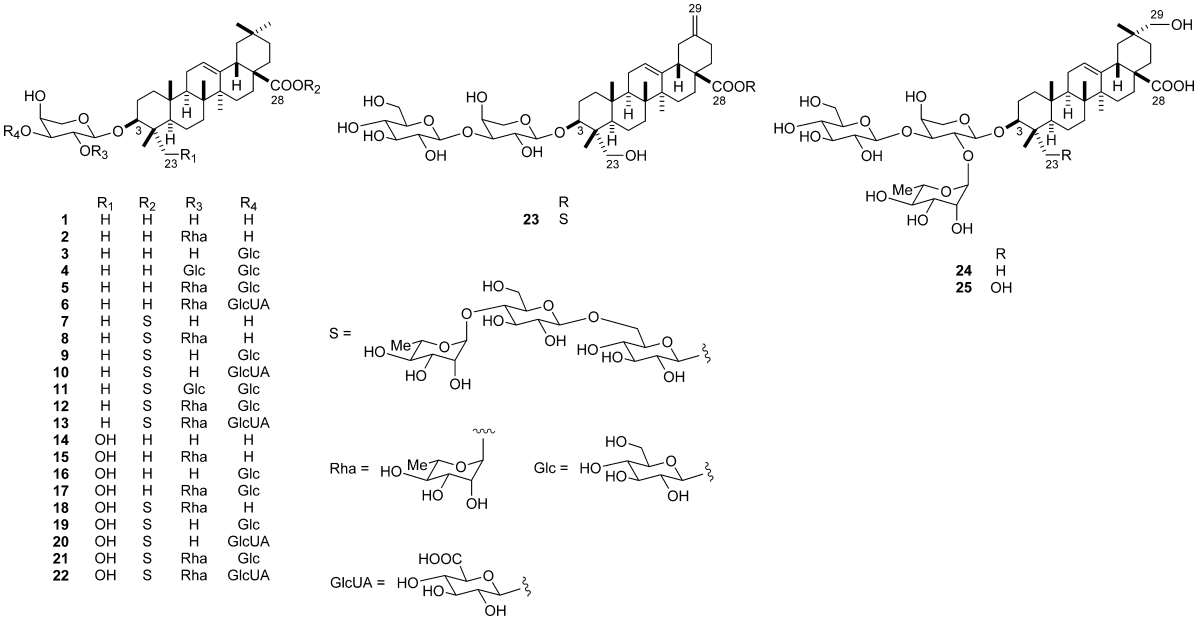

glucopyranosyl-(1→6)-β-D-glucopyranosyl ester (**18**),[10] 3β-[(*O*-β-D-glucopyranosyl-(1→3)-α-L-arabinopyranosyl)oxy]-23-hydroxyolean-12-en-28-oic acid *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester (**19**),[12] 3β-[(*O*-β-D-glucopyranosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl)oxy]-23-hydroxyolean-12-en-28-oic acid *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester (**21**),[10] and 3β-[(*O*-β-D-glucopyranosyl-(1→3)-α-L-arabinopyranosyl)oxy]-23-hydroxy-30-noroleana-12,20(29)-dien-28-oic acid *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester (**23**),[13] respectively.

Compound **10** was isolated as an amorphous solid and showed an accurate $[M+Na]^+$ ion at *m/z* 1257.5906 in the high-resolution electron-spray-ionization time of flight mass spectrum (HR-ESI-TOF-MS), corresponding to the empirical molecular formula $C_{59}H_{94}O_{27}$. The IR spectrum of **10** was suggestive of a glycoside (3382, 1065 cm^{-1}) and indicated the presence of carbonyl groups (1731, 1605 cm^{-1}) in the molecule. The ^{1}H-NMR spectrum of **1** showed signals due to seven quaternary methyl groups at δ 1.28, 1.25, 1.09, 0.98, 0.90×2, and 0.88 (each s), an olefinic proton at δ 5.41 (br s), and five anomeric protons at δ 6.23 (d, J=8.0 Hz), 5.84 (br s), 5.41 (d, J=7.0 Hz), 4.98 (d, J=7.7 Hz), and 4.75 (d, J=6.8 Hz). The ^{13}C-NMR spectrum revealed signals for six quaternary carbons at δ 47.0, 42.1, 39.9, 39.6, 37.0, and 30.7, an oxygen-bearing methine carbon at δ 88.6, a set of olefinic carbons at δ 144.1 and 122.8, two carbonyl carbons at δ 176.5 and 172.8, and five anomeric carbons at δ 107.2, 106.1, 104.8, 102.7, and 95.6. Acid hydrolysis of **10** with 1.0 M HCl yielded 3β-hydroxyolean-12-en-28-oic acid (oleanolic acid), and L-arabinose, D-glucose, D-glucuronic acid, and L-rhamnose as the carbohydrate moieties. These sugars, including their absolute configurations, were identified by direct HPLC analysis of the hydrolysate, which was performed on an aminopropyl-bonded silica gel column for the identification of L-arabinose, D-glucose, and L-rhamnose, and a sulfonated polystyrene ion-exclusion column for the identification of D-glucuronic acid. The C-3 oxymethine carbon and C-28 carbonyl carbon were observed at δ 88.6 and 176.5, respectively, in the ^{13}C-NMR spectrum of **10**, which suggests that **10** is a 3,28-bisdesmoside of oleanolic acid. Analysis of the ^{1}H–^{1}H shift correlation spectroscopy (COSY) and totally correlated spectroscopy (TOCSY) allowed the sequential assignments of the ^{1}H-NMR signals arising from the five monosaccharides. Their signal multiplet patterns and coupling constants (Table 1) indicated the presence of an α-L-arabinopyranosyl ($^4C_1$) unit (Ara), two β-D-glucopyranosyl ($^4C_1$) units (Glc and Glc′), a β-D-glucuronopyranosyl ($^4C_1$) unit (GlcUA), and an α-L-rhamnopyranosyl ($^1C_4$) unit (Rha) in **10**. All the proton signals for the sugar moieties were associated with one-bond coupled carbon signals using the ^{1}H-detected heteronuclear multiple-quantum coherence (HMQC) spectrum. The GlcUA and Rha residues were considered to be the terminal units, as shown by the absence of any glycosylation shifts for their carbon signals, while the C-3 hydroxy group of the Ara unit, the C-4 of the glucosyl unit (Glc′), and the C-6 of the other glucosyl unit (Glc) were suggested to be substituted by comparison of the ^{13}C-NMR shifts with those reported in the literature.[14] In the ^{1}H-detected heteronuclear multiple-bond connectivity (HMBC) spectrum, the H-1 proton at δ 5.41 (GlcUA) showed a long-range correlation with C-3 (δ 84.1) of the Ara moiety, of which the H-1 proton at δ 4.75 in turn showed an HMBC correlation with C-3 (δ 88.6) of the aglycone. On the other hand, long-range correlations between the H-1 proton of the Rha moiety at δ 5.84 and C-4 of the Glc′ moiety at δ 78.2, the H-1 proton of the Glc′ moiety at δ 4.98 and C-6 of the Glc moiety at δ 69.1, and between the H-1 proton of the Glc moiety at δ 6.23 and C-28 of the aglycone at δ 176.5 could be observed. Accordingly, the structure of **10** was formulated as 3β-[(*O*-β-D-glucuronopyranosyl-(1→3)-α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester.

Table 1. ^{1}H- and ^{13}C-NMR Spectral Data for the Sugar Moieties of **10**, **13**, and **24** in C_5D_5N

10					**13**					**24**				
Positions		δ_H	J (Hz)	δ_C	Positions		δ_H	J (Hz)	δ_C	Positions		δ_H	J (Hz)	δ_C
Ara	1′	4.75 d	6.8	107.2	Ara	1′	4.83 d	5.8	104.8	Ara	1′	4.86 d	5.6	104.8
	2′	4.58 dd	8.5, 6.8	71.6		2′	4.64 dd	8.7, 5.8	74.6		2′	4.65 dd	7.5, 5.6	74.7
	3′	4.24 br d	8.5	84.1		3′	4.31 dd	8.7, 2.8	82.6		3′	4.33 br d	7.5	82.2
	4′	4.49 br s		68.9		4′	4.56 m		68.4		4′	4.54 br s		68.2
	5′ a	4.23 br d	11.4	66.8		5′ a	4.19 br d	10.0	65.1		5′ a	4.23 dd	11.8, 4.5	64.9
	b	3.76 br d	11.4			b	3.71 br d	10.0			b	3.75 dd	11.8, 1.6	
GlcUA	1″	5.41 d	7.0	106.1	Rha	1″	6.15 br s		101.9	Rha	1″	6.16 br s		101.9
	2″	4.06 dd	8.0, 7.0	75.3		2″	4.74 br d	3.4	72.2		2″	4.74 br d	3.1	72.4
	3″	4.31 m		77.7		3″	4.59 dd	9.4, 3.4	72.4		3″	4.60 dd	9.4, 3.1	72.5
	4″	4.46 dd	8.9, 8.9	73.4		4″	4.26 dd	9.4, 9.4	73.8		4″	4.28 dd	9.4, 9.4	73.9
	5″	4.57 d	8.9	77.4		5″	4.59 dq	9.4, 6.1	69.8		5″	4.59 dq	9.4, 6.2	70.0
	6″	—		172.8		6″	1.60 d	6.1	18.4		6″	1.64 d	6.2	18.6
Glc	1‴	6.23 d	8.0	95.6	GlcUA	1‴	5.20 d	7.7	104.9	Glc	1‴	5.11 d	7.8	104.7
	2‴	4.13 dd	8.6, 8.0	73.8		2‴	3.99 dd	8.4, 7.7	74.6		2‴	3.95 dd	8.8, 7.8	75.0
	3‴	4.23 dd	8.6, 8.6	78.7		3‴	4.28 dd	9.3, 8.4	77.5		3‴	4.17 dd	8.8, 8.8	78.3
	4‴	4.31 dd	8.6, 8.6	70.8		4‴	4.47 dd	9.3, 9.3	73.2		4‴	4.19 dd	8.8, 8.8	71.4
	5‴	4.10 m		78.0		5‴	4.61 d	9.3	77.4		5‴	3.93 m		78.6
	6‴ a	4.66 br d	9.9	69.1		6‴	—		172.7		6‴ a	4.50 dd	11.6, 1.9	62.5
	b	4.31 m									b	4.33 dd	11.6, 4.6	
Glc′	1⁗	4.98 d	7.7	104.8	Glc	1⁗	6.20 d	8.1	95.5					
	2⁗	3.94 dd	9.3, 7.7	75.3		2⁗	4.12 dd	9.0, 8.1	73.8					
	3⁗	4.14 dd	9.3, 9.3	76.5		3⁗	4.22 dd	9.0, 9.0	78.6					
	4⁗	4.40 dd	9.3, 9.3	78.2		4⁗	4.31 dd	9.0, 9.0	70.7					
	5⁗	3.65 br dd	9.3, 3.3	77.1		5⁗	4.08 m		77.9					
	6⁗ a	4.20 br d	11.8	61.2		6⁗ a	4.65 dd	11.7, 3.0	69.1					
	b	4.08 dd	11.8, 3.3			b	4.29 m							
Rha	1⁗′	5.84 br s		102.7	Glc′	1⁗′	4.97 d	7.8	104.8					
	2⁗′	4.67 br d	3.0	72.5		2⁗′	3.91 dd	9.2, 7.8	75.2					
	3⁗′	4.54 dd	9.4, 3.0	72.7		3⁗′	4.12 dd	9.2, 9.2	76.4					
	4⁗′	4.32 dd	9.4, 9.4	74.0		4⁗′	4.36 dd	9.2, 9.2	78.1					
	5⁗′	4.95 dq	9.4, 6.1	70.3		5⁗′	3.63 br dd	9.2, 3.2	77.0					
	6⁗′	1.69 d	6.1	18.5		6⁗′ a	4.18 br d	11.9	61.1					
						b	4.07 dd	11.9, 3.2						
					Rha′	1⁗″	5.81 br s		102.6					
						2⁗″	4.66 br d	3.3	72.4					
						3⁗″	4.53 dd	9.3, 3.3	72.6					
						4⁗″	4.31 dd	9.3, 9.3	73.9					
						5⁗″	4.91 dq	9.3, 6.2	70.2					
						6⁗″	1.66 d	6.2	18.5					

Compound **13**, obtained as an amorphous solid, had a molecular formula of $C_{65}H_{104}O_{31}$ on the basis of its HR-ESI-TOF-MS. The deduced molecular formula was higher than that of **10** by $C_6H_{10}O_4$, indicating the presence of one more deoxyhexosyl unit in **13**. The ^{1}H-NMR spectrum of **13** showed signals for six anomeric protons at δ 6.20 (d, J=8.1 Hz), 6.15 (br s), 5.81 (br s), 5.20 (d, J=7.7 Hz), 4.97 (d, J=7.8 Hz), and 4.83 (d, J=5.8 Hz), and the two methyl groups of two deoxyhexose units at δ 1.66 (d, J=6.2 Hz) and 1.60 (d, J=6.1 Hz), as well as signals for seven tertiary methyl groups at δ 1.22, 1.20, 1.11, 1.06, 0.86×2, and 0.84 (each s). Six anomeric carbons were observed at δ 104.9, 104.8×2, 102.6, 101.9, and 95.5 in the ^{13}C-NMR spectrum of **13**. Acid hydrolysis of **13** with 1.0 M HCl yielded oleanolic acid, L-arabinose, D-glucose, D-glucuronic acid, and L-rhamnose. On comparison of the whole ^{13}C-NMR spectrum of **13** with that of **10**, the signals due to the aglycone moiety and the triglycoside residue linked to C-28 of the aglycone were observed at almost the same positions in the two compounds. However, a set of six additional signals corresponding to a terminal α-L-rhamnopyranosyl group appeared at δ 101.9 (CH), 72.2 (CH), 72.4 (CH), 73.8 (CH), 69.8 (CH), and 18.5 (Me), and the signal due to C-2 of the arabinosyl unit attached to C-3 of the aglycone was displaced downfield by 3.0 ppm and observed at δ 74.6, suggesting that the C-2 position of the arabinosyl moiety is glycosylated by the additional L-rhamnosyl unit. This was consistent with the fact that the product obtained by alkaline hydrolysis of **13** with 4% KOH in EtOH, through which the ester linkage of the triglycoside to C-28 of the aglycone was cleaved, was identical to the known compound **6**. Confirmative evidence for the sugar sequences of **13** was found in the HMBC spectrum, in which long-range correlations were observed from each anomeric proton across the glycosidic bond to the carbon of another substituted monosaccharide or aglycone (Fig. 1). The structure of **13** was established to be 3β-[(O-β-D-glucuronopyranosyl-(1→3)-O-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl)oxy]olean-12-en-28-oic acid O-α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester.

Compound **20** was shown to have the molecular formula $C_{59}H_{94}O_{28}$ on the basis of the HR-ESI-TOF-MS data. Comparison of the ^{1}H- and ^{13}C-NMR spectra of **20** with those of **10** showed considerable structural similarity. However, the

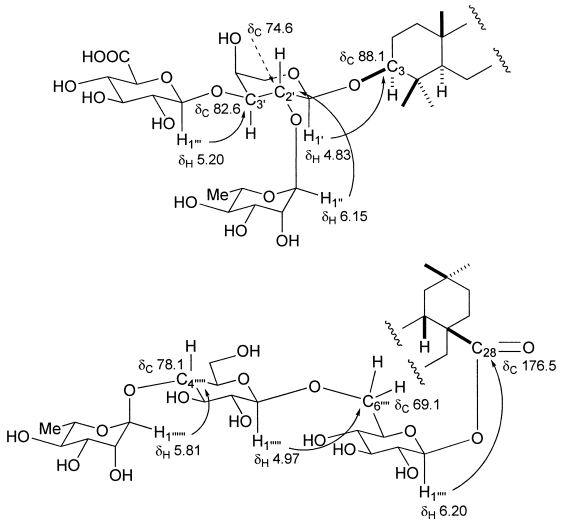

Fig. 1. HMBC Correlations of the Glycoside Moieties of **13**

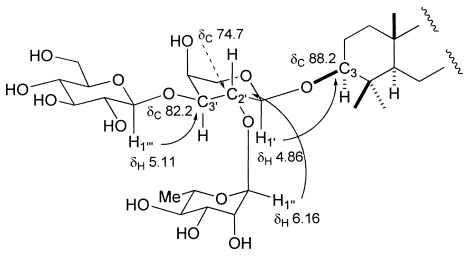

Fig. 2. HMBC Correlations of the Glycoside Moiety of **24**

molecular formula of **20** was higher by one oxygen atom than that of **10**. In the ^{13}C-NMR spectrum, the signal due to the C-23 methyl group, which was observed at δ 28.1 in **10**, was displayed by a signal due to a hydroxymethyl carbon at δ 64.1. Furthermore, the ABq signal at δ 4.33 and 3.70 (J=10.7 Hz) was associated with the hydroxymethyl carbon signal by the HMQC spectrum. All other signals, including the signals due to the two sugar moieties attached to C-3 and C-28 of the aglycone, were almost completely superimposable between **10** and **20**. Acid hydrolysis of **20** gave 3β,23-dihydroxyolean-12-en-28-oic acid (hederagenin), L-arabinose, D-glucose, D-glucuronic acid, and L-rhamnose. On the basis of these data, the structure of **20** was determined to be 3β-[(*O*-β-D-glucuronopyranosyl-(1→3)-α-L-arabinopyranosyl)oxy]-23-hydroxyolean-12-en-28-oic acid *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester.

Compound **22** was analyzed for $C_{65}H_{104}O_{32}$ based on the HR-ESI-TOF-MS data. The ^{1}H- and ^{13}C-NMR spectral properties of **22** were closely related to those of **20**, except for the presence of signals due to an additional terminal α-L-rhamnopyranosyl group, which was revealed to be linked to C-3 of the arabinosyl unit attached to C-3 of the aglycone in the HMBC data. Furthermore, the ^{1}H- and ^{13}C-NMR signals attributable to the sugar moieties were in good agreement with those of **13**. Acid hydrolysis of **22** gave hederagenin, L-arabinose, D-glucose, D-glucuronic acid, and L-rhamnose. Thus the structure of **22** was shown to be 3β-[(*O*-β-D-glucuronopyranosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl)oxy]-23-hydroxyolean-12-en-28-oic acid *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester.

Compound **24** was deduced to be $C_{47}H_{76}O_{17}$ from the HR-ESI-TOF-MS data. The ^{1}H-NMR spectroscopic data of **24** showed signals for three anomeric protons at δ 6.16 (br s), 5.11 (d, J=7.8 Hz), and 4.86 (d, J=5.6 Hz), as well as signals for six methyl groups at δ 1.32, 1.22, 1.21, 1.12, 1.00, and 0.84 (each s), and an olefinic proton at δ 5.51 (br s). The carbonyl carbon signal due to C-28 was observed at δ 180.2, which suggests that no sugar is linked to the C-28 carboxyl group. These spectral properties of **24** were essentially analogous to those of **5**. However, the molecular formula of **24** was higher by one oxygen atom than that of **5**, and the NMR signals arising from the ring E part of **24** were different from those of **5**, especially in the lack of a methyl singlet due to Me-29 or Me-30 in **24**. Acid hydrolysis of **24** gave 3β,29-dihydroxyolean-12-en-28-oic acid,[15] L-arabinose, D-glucose, and L-rhamnose. The triglycoside attached to C-3 of the aglycone was confirmed to be the same as that of **5** based on the HMBC spectrum of **24** (Fig. 2). The structure of **24** was determined to be 3β-[(*O*-β-D-glucopyranosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl)oxy]-29-hydroxyolean-12-en-28-oic acid.

Compound **25** was assigned the molecular formula $C_{47}H_{76}O_{18}$ using HR-ESI-TOF-MS. The ^{1}H-NMR spectrum of **25** showed signals for tertiary methyl groups at δ 1.24, 1.21, 1.09, 1.03, and 0.93 (each s), an olefinic proton at δ 5.50 (br s), and three anomeric protons at δ 6.23 (br s), 5.07 (d, J=6.4 Hz), and 5.04 (d, J=7.8 Hz). These ^{1}H-NMR data, together with the deduced molecular formula of **25**, which was higher by one oxygen atom than that of **24**, and the ^{13}C-NMR information, suggest that the aglycone moiety of **25** has one more hydroxy group than that of **24**. Acid hydrolysis of **25** resulted in the production of 3β,23,29-trihydroxyolean-12-en-28-oic acid,[16] L-arabinose, D-glucose, and L-rhamnose. The triglycoside attached to C-3 of the aglycone was ascertained to be the same as that of **5** and **24** by analysis of the HMBC spectrum of **25**. The structure of **25** was established to be 3β-[(*O*-β-D-glucopyranosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl)oxy]-23,29-dihydroxyolean-12-en-28-oic acid.

Compounds **10**, **13**, **20**, and **22** are new triterpene bisdesmosides with a terminal glucuronic acid moiety as a sugar unit, and **24** and **25** are new triterpene monodesmosides, of which the aglycone has a hydroxy group at C-29. Our previous chemical study of the stems of *A. trifoliate* resulted in the isolation of a total of 25 triterpene and triterpene glycosides, among which the main triterpene glycosides were monodesmosides with one sugar unit at C-28 of the aglycone.[1] In this study, **8**, **12**, **18**, and **19**, which are bisdesmosides with two sugar units at C-3 and C-28 of the aglycone, have been shown to be the main triterpene glycosides contained in the stems of *A. quinata*. It may be possible to distinguish between *A. quinata* and *A. trifoliate* chemically by a comparison of their triterpene glycoside constituents.

Experimental

Optical rotations were measured using a JASCO DIP-360 (Tokyo, Japan) automatic digital polarimeter. IR spectra were recorded on a JASCO FT-IR 620 spectrophotometer. NMR spectra were recorded on a Bruker DRX-500 spectrometer (500 MHz for ^{1}H-NMR, Karlsruhe, Germany) using standard Bruker pulse programs. Chemical shifts are given as the δ-value with refer-

ence to tetramethylsilane (TMS) as an internal standard. ESI-TOF-MS data were obtained on a Micromass LCT mass spectrometer (Manchester, U.K.). Diaion HP-20 (Mitsubishi-Chemical, Tokyo, Japan), Sephadex LH-20 (Pharmacia, Uppsala, Sweden), silica gel (Fuji-Silysia Chemical, Aichi, Japan), and octadecylsilanized (ODS) silica gel (Nacalai Tesque, Kyoto, Japan) were used for column chromatography. TLC was carried out on precoated Kieselgel 60 F_{254} (0.25 mm, Merck, Darmstadt, Germany) and RP-18 F_{254} S (0.25 mm thick, Merck) plates, and spots were visualized by spraying with 10% H_2SO_4 followed by heating. HPLC was performed using a system comprised of a CCPM pump (Tosoh, Tokyo, Japan), a CCP PX-8010 controller (Tosoh), an RI-8010 detector (Tosoh) and a Shodex OR-2 detector (Showa-Denko, Tokyo, Japan), and a Rheodyne injection port.

Plant Material The stems of *A. quinata* were collected in the fields of Shiojiri ward, Nagano, Japan, in October 2000. The plant was identified by Dr. Yutaka Sashida, emeritus professor of the Tokyo University of Pharmacy and Life Sciences. A voucher specimen has been deposited in our laboratory (voucher No. 00-10-08-AQ, Laboratory of Medicinal Pharmacognosy).

Extraction and Isolation The plant material (dry weight 2.0 kg) was extracted with hot MeOH twice (each 4.6 l). The extract was concentrated under residual pressure, and the viscous concentrate (215 g) was passed through a Diaion HP-20 column (80 mm i.d.×400 mm), successively eluted with 30% MeOH, EtOH, and EtOAc (each 3 l). The EtOH eluate portion (60 g) was chromatographed on silica gel (80 mm i.d.×300 mm) and eluted with $CHCl_3$–MeOH–H_2O gradients (40 : 10 : 1; 20 : 10 : 1; 7 : 4 : 1; 5 : 5 : 1) and finally with MeOH alone, to give 10 fractions (I—X). Fraction I was subjected to column chromatography on ODS silica gel (30 mm i.d.×150 mm) eluted with MeOH–H_2O (9 : 2), silica gel (30 mm i.d.×180 mm) with $CHCl_3$–MeOH (19 : 1), and on Sephadex LH-20 (30 mm i.d.×200 mm) using MeOH to yield **1** (4.5 mg) and **14** (26.8 mg). Fraction II was subjected to silica gel column chromatography (35 mm i.d.×200 mm) eluted with $CHCl_3$–MeOH–H_2O (40 : 10 : 1) to give **2** (15.3 mg), **3** (11.9 mg), and **15** (20.6 mg). Fraction III was subjected to column chromatography on silica gel (60 mm i.d.×250 mm) eluted with $CHCl_3$–MeOH–H_2O (25 : 10 : 1), ODS silica gel (30 mm i.d.×150 mm) with MeCN–H_2O (4 : 5), and on Sephadex LH-20 (40 mm i.d.×250 mm) using MeOH to yield **16** (27.6 mg). Fraction IV was separated by a silica gel column (60 mm i.d.×250 mm) eluted with $CHCl_3$–MeOH–H_2O (30 : 10 : 1; 20 : 10 : 1) to give four subfractions (IVa—IVd). Fraction IVa was chromatographed on ODS silica gel (40 mm i.d.×230 mm) eluted with MeCN–H_2O (4 : 5) to afford **5** (22.3 mg), **17** (146 mg), and **24** (10.8 mg). Fraction IVb was purified by an ODS silica gel column (35 mm i.d.×180 mm) eluted with MeCN–H_2O (5 : 6) to furnish **4** (12.3 mg). Fraction IVc was subjected to column chromatography on silica gel (25 mm i.d.×200 mm) eluted with $CHCl_3$–MeOH–H_2O (50 : 20 : 1) and ODS silica gel (20 mm i.d.×150 mm) with MeCN–H_2O (4 : 9) to furnish **25** (25.7 mg). Fraction IVd was subjected to an ODS silica gel column (30 mm i.d.×200 mm) eluted with MeCN–H_2O (2 : 3) to yield **6** (20.4 mg). Fraction V was subjected to column chromatography on ODS silica gel (60 mm i.d.×200 mm) eluted with MeCN–H_2O (1 : 2) and silica gel (40 mm i.d.×200 mm) with $CHCl_3$–MeOH–H_2O (12 : 5 : 1) to give **7** (123 mg) and **8** (1.51 g). Fraction VI was subjected to an ODS silica gel column (60 mm i.d.×250 mm) eluted with MeCN–H_2O (4 : 9) to yield **9** (278 mg), **10** (126 mg), **18** (1.58 g), and **19** (919 mg). Fraction VII was chromatographed on ODS silica gel (45 mm i.d.×250 mm) eluted with MeCN–H_2O (1 : 3) and silica gel (40 mm i.d.×200 mm) with $CHCl_3$–MeOH–H_2O (7 : 4 : 1) to afford **20** (112 mg) and **23** (94.0 mg). Fraction VIII was subjected to column chromatography on ODS silica gel (50 mm i.d.×200 mm) eluted with MeCN–H_2O (1 : 2) and silica gel (25 mm i.d.×200 mm) with EtOAc–MeOH–H_2O (10 : 5 : 1) to yield **11** (32.6 mg), **12** (3.11 g), **13** (44.8 mg), and **21** (97.3 mg). Fraction IX was purified by silica gel column chromatography (40 mm i.d.×200 mm) eluted with $CHCl_3$–MeOH–H_2O (14 : 10 : 1) and ODS silica gel column chromatography (30 mm i.d.×200 mm) with MeOH–H_2O (1 : 1) to furnish **22** (119 mg).

Compound **10**: Amorphous solid, $[\alpha]_D^{27}$ −16.0° (c=0.10, MeOH). HR-ESI-TOF-MS (positive mode) m/z: 1257.5906 $[M+Na]^+$ (Calcd for $C_{59}H_{94}O_{27}Na$: 1257.5880). IR (film) ν_{max} cm^{-1}: 3382 (OH), 2928 (CH), 1731 and 1605 (C=O), 1065. ^{1}H-NMR (C_5D_5N) δ: 5.41 (1H, br s, H-12), 3.34 (1H, dd, J=11.6, 3.8 Hz, H-3), 3.18 (1H, dd, J=13.4, 3.2 Hz, H-18), 1.28 (3H, s, Me-23), 1.25 (3H, s, Me-27), 1.09 (3H, s, Me-26), 0.98 (3H, s, Me-24), 0.90 (3H×2, Me-29 and Me-30), 0.88 (3H, s, Me-25); signals for the sugar moieties, see Table 1. ^{13}C-NMR (C_5D_5N) δ: 38.8 (C-1), 26.6 (C-2), 88.6 (C-3), 39.6 (C-4), 55.8 (C-5), 18.5 (C-6), 33.1 (C-7), 39.9 (C-8), 48.0 (C-9), 37.0 (C-10), 23.8 (C-11), 122.8 (C-12), 144.1 (C-13), 42.1 (C-14), 28.2 (C-15), 23.3 (C-16), 47.0 (C-17), 41.6 (C-18), 46.2 (C-19), 30.7 (C-20), 34.0 (C-21), 32.5 (C-22), 28.1 (C-23), 16.9 (C-24), 15.6 (C-25), 17.5 (C-26), 26.0 (C-27), 176.5 (C-28), 33.1 (C-29), 23.7 (C-30); signals for the sugar moieties, see Table 1.

Acid Hydrolysis of 10 A solution of **10** (24.1 mg) in 1.0 M HCl (dioxane–H_2O, 1 : 1, 2 ml) was heated at 95 °C for 2 h under an Ar atmosphere. After dilution of the reaction mixture with H_2O (5 ml), it was extracted with EtOAc (10 ml×3). The EtOAc extract was subjected to a silica gel column (20 mm i.d.×140 mm) eluted with $CHCl_3$–MeOH (19 : 1) to give oleanolic acid (5.8 mg). The H_2O residue was neutralized by adding $AgCO_3$. The mixture was filtered and then passed through a Sep-Pak C18 cartridge (Waters, Milford, MA, U.S.A.) eluted with H_2O (6 ml) to give a sugar fraction (11.5 mg). The sugar fraction was analyzed with HPLC under the following conditions: 1) column, Aminex HPX-87H (7.8 mm i.d.×300 mm, 5 μm, Bio-Rad Laboratories, Hercules, CA, U.S.A.); solvent, 5 mM H_2SO_4; flow rate, 0.6 ml/min; detection, refractive index (RI) and optical rotation (OR); and t_R (min): 8.18 (D-glucuronic acid, positive optical rotation) and 9.08 (D-glucose, positive optical rotation); 2) column, Capcell Pak NH2 UG80 (4.6 mm i.d.×250 mm, 5 μm, Shiseido, Tokyo, Japan); solvent, MeCN–H_2O (17 : 3); flow rate, 1.0 ml/min; detection, RI and OR; and t_R (min): 6.41 (L-rhamnose, negative optical rotation), 7.50 (L-arabinose, positive optical rotation), and 12.06 (D-glucose, positive optical rotation).

Compound **13**: Amorphous solid, $[\alpha]_D^{25}$ −24.0° (c=0.10, MeOH). HR-ESI-TOF-MS (positive mode) m/z: 1426.6339 $[M+2Na]^+$ (Calcd for $C_{65}H_{104}O_{31}Na_2$: 1426.6356). IR (film) ν_{max} cm^{-1}: 3383 (OH), 2927 (CH), 1728 and 1598 (C=O), 1065. ^{1}H-NMR (C_5D_5N) δ: 5.38 (1H, t-like, J=3.5 Hz, H-12), 3.29 (1H, dd, J=11.5, 3.9 Hz, H-3), 3.14 (1H, dd, J=13.5, 3.8 Hz, H-18), 1.22 (3H, s, Me-27), 1.20 (3H, s, Me-23), 1.11 (3H, s, Me-24), 1.06 (3H, s, Me-26), 0.86 (3H×2, s, Me-29 and Me-30), 0.84 (3H, s, Me-25); signals for the sugar moieties, see Table 1. ^{13}C-NMR (C_5D_5N) δ: 38.9 (C-1), 26.5 (C-2), 88.1 (C-3), 39.5 (C-4), 55.9 (C-5), 18.4 (C-6), 33.0 (C-7), 39.8 (C-8), 48.0 (C-9), 36.9 (C-10), 23.7 (C-11), 122.7 (C-12), 144.0 (C-13), 42.0 (C-14), 28.2 (C-15), 23.3 (C-16), 46.9 (C-17), 41.6 (C-18), 46.1 (C-19), 30.6 (C-20), 33.9 (C-21), 32.4 (C-22), 28.0 (C-23), 17.0 (C-24), 15.6 (C-25), 17.4 (C-26), 26.0 (C-27), 176.5 (C-28), 33.0 (C-29), 23.6 (C-30); signals for the sugar moieties, see Table 1.

Acid Hydrolysis of 13 Compound **13** (21.0 mg) was subjected to acid hydrolysis as described for **10** to give oleanolic acid (5.2 mg) and a sugar fraction (8.8 mg). HPLC analysis of the sugar fraction under the same conditions as in the case of **10** resulted in identification of L-arabinose, D-glucose, D-glucuronic acid, and L-rhamnose.

Alkaline Hydrolysis of 13 Compound **13** (5.0 mg) was treated with 4% KOH in EtOH (3 ml) at 80 °C for 2 h. The reaction mixture was neutralized by passage through an Amberlite IR-120B (Organo, Tokyo, Japan) and chromatographed on silica gel (15 mm i.d.×130 mm) eluted with $CHCl_3$–MeOH–H_2O (20 : 10 : 1) to give **6** (0.8 mg).

Compound **20**: Amorphous solid, $[\alpha]_D^{24}$ −3.1° (c=0.13, MeOH). HR-ESI-TOF-MS (positive mode) m/z: 1273.5746 $[M+Na]^+$ (Calcd for $C_{59}H_{94}O_{28}Na$: 1273.5829). IR (film) ν_{max} cm^{-1}: 3381 (OH), 2925 (CH), 1732 and 1609 (C=O), 1062. ^{1}H-NMR (C_5D_5N) δ: 6.23 (1H, d, J=7.4 Hz, H-1‴), 5.85 (1H, br s, H-1⁗), 5.42 (1H, d, J=7.6 Hz, H-1″), 5.39 (1H, br s, H-12), 4.98 (1H, d, J=7.8 Hz, H-1⁗), 4.97 (1H, d, J=6.9 Hz, H-1′), 4.33 (1H, d, J=10.7 Hz, H-23a), 4.28 (1H, dd, J=12.5, 3.6 Hz, H-3), 3.70 (1H, d, J=10.7 Hz, H-23b), 3.16 (1H, dd, J=13.8, 3.2 Hz, H-18), 1.69 (3H, d, J=6.1 Hz, Me-6⁗), 1.17 (3H, s, Me-27), 1.11 (3H, s, Me-26), 0.95 (3H, s, Me-25), 0.94 (3H, Me-24), 0.87 (3H, s, Me-30), 0.86 (3H, s, Me-29). ^{13}C-NMR (C_5D_5N) δ: 38.8 (C-1), 26.2 (C-2), 81.7 (C-3), 43.5 (C-4), 47.4 (C-5), 18.1 (C-6), 32.7 (C-7), 39.9 (C-8), 48.1 (C-9), 36.9 (C-10), 23.8 (C-11), 122.9 (C-12), 144.1 (C-13), 42.1 (C-14), 28.2 (C-15), 23.3 (C-16), 47.0 (C-17), 41.6 (C-18), 46.1 (C-19), 30.7 (C-20), 33.9 (C-21), 32.5 (C-22), 64.1 (C-23), 13.6 (C-24), 16.1 (C-25), 17.5 (C-26), 26.0 (C-27), 176.5 (C-28), 33.0 (C-29), 23.6 (C-30), 106.6 (C-1′), 71.9 (C-2′), 84.0 (C-3′), 69.2 (C-4′), 67.1 (C-5′), 106.4 (C-1″), 75.3 (C-2″), 77.7 (C-3″), 73.3 (C-4″), 77.8 (C-5″), 172.8 (C-6″), 95.6 (C-1‴), 73.8 (C-2‴), 78.6 (C-3‴), 70.8 (C-4‴), 78.0 (C-5‴), 69.1 (C-6‴), 104.8 (C-1⁗), 75.3 (C-2⁗), 76.4 (C-3⁗), 78.2 (C-4⁗), 77.1 (C-5⁗), 61.2 (C-6⁗), 102.7 (C-1⁗), 72.5 (C-2⁗), 72.7 (C-3⁗), 73.9 (C-4⁗), 70.3 (C-5⁗), 18.5 (C-6⁗).

Acid Hydrolysis of 20 Compound **20** (22.2 mg) was subjected to acid hydrolysis as described for **10** to give hederagenin (5.0 mg) and a sugar fraction (12.4 mg). HPLC analysis of the sugar fraction under the same conditions as in the case of **10** resulted in identification of L-arabinose, D-glucose, D-glucuronic acid, and L-rhamnose.

Compound **22**: Amorphous solid, $[\alpha]_D^{24}$ −10.0° (c=0.10, MeOH). HR-ESI-TOF-MS (positive mode) m/z: 1419.6418 $[M+Na]^+$ (Calcd for $C_{65}H_{104}O_{32}Na$: 1419.6408). IR (film) ν_{max} cm^{-1}: 3363 (OH), 2925 (CH), 1731 and 1590 (C=O), 1060. ^{1}H-NMR (C_5D_5N) δ: 6.23 (1H, d, J=7.9 Hz,

H-1‴″), 6.22 (1H, br s, H-1″), 5.84 (1H, br s, H-1⁗″), 5.39 (1H, br s, H-12), 5.10 (1H, d, J=7.6 Hz, H-1‴), 5.07 (1H, d, J=6.3 Hz, H-1′), 4.99 (1H, d, J=7.8 Hz, H-1⁗″), 4.28 (1H, m, H-3), 4.17 (1H, d, J=10.5 Hz, H-23a), 3.76 (1H, d, J=10.5 Hz, H-23b), 3.15 (1H, dd, J=13.4, 3.4 Hz, H-18), 1.69 (3H, d, J=6.2 Hz, Me-6⁗″), 1.64 (3H, d, J=6.1 Hz, Me-6″), 1.17 (3H, s, Me-27), 1.10 (3H×2, s, Me-24 and Me-26), 0.96 (3H, s, Me-25), 0.87 (3H, s, Me-30), 0.85 (3H, s, Me-29). ^{13}C-NMR (C_5D_5N) δ: 39.1 (C-1), 26.3 (C-2), 80.5 (C-3), 43.5 (C-4), 47.7 (C-5), 18.1 (C-6), 32.8 (C-7), 39.9 (C-8), 48.2 (C-9), 36.9 (C-10), 23.8 (C-11), 122.9 (C-12), 144.0 (C-13), 42.1 (C-14), 28.3 (C-15), 23.3 (C-16), 47.0 (C-17), 41.6 (C-18), 46.1 (C-19), 30.7 (C-20), 33.9 (C-21), 32.5 (C-22), 63.8 (C-23), 14.0 (C-24), 16.2 (C-25), 17.5 (C-26), 26.0 (C-27), 176.5 (C-28), 33.0 (C-29), 23.6 (C-30), 104.3 (C-1′), 74.5 (C-2′), 83.6 (C-3′), 68.9 (C-4′), 65.8 (C-5′), 101.8 (C-1″), 72.3 (C-2″), 72.5 (C-3″), 74.0 (C-4″), 69.8 (C-5″), 18.5 (C-6″), 105.2 (C-1‴), 74.7 (C-2‴), 77.6 (C-3‴), 73.3 (C-4‴), 77.4 (C-5‴), 172.9 (C-6‴), 95.6 (C-1⁗″), 73.8 (C-2⁗″), 78.7 (C-3⁗″), 70.8 (C-4⁗″), 78.0 (C-5⁗″), 69.2 (C-6⁗″), 104.8 (C-1⁗″), 75.3 (C-2⁗″), 76.5 (C-3⁗″), 78.2 (C-4⁗″), 77.1 (C-5⁗″), 61.2 (C-6⁗″), 102.7 (C-1⁗″), 72.5 (C-2⁗″), 72.7 (C-3⁗″), 74.0 (C-4⁗″), 70.3 (C-5⁗″), 18.5 (C-6⁗″).

Acid Hydrolysis of 22 Compound **22** (24.4 mg) was subjected to acid hydrolysis as described for **10** to give hederagenin (2.9 mg) and a sugar fraction (9.7 mg). HPLC analysis of the sugar fraction under the same conditions as in the case of **10** resulted in identification of L-arabinose, D-glucose, D-glucuronic acid, and L-rhamnose.

Compound **24**: Amorphous solid, $[\alpha]_D^{25}$ −1.4° (c=0.11, MeOH). HR-ESI-TOF-MS (positive mode) m/z: 935.5070 $[M+Na]^+$ (Calcd for $C_{47}H_{76}O_{17}Na$: 935.4979). IR (film) ν_{max} cm^{-1}: 3389 (OH), 2933 (CH), 1695 (C=O), 1072. ^{1}H-NMR (C_5D_5N) δ: 5.51 (1H, br s, H-12), 3.61 (2H, s, H_2-29), 3.29 (1H, dd, J=11.7, 4.1 Hz, H-3), 3.42 (1H, dd, J=13.5, 3.9 Hz, H-18), 1.32 (3H, s, Me-27), 1.22 (3H, s, Me-30), 1.21 (3H, s, Me-23), 1.12 (3H, s, Me-24), 1.00 (3H, s, Me-26), 0.84 (3H, s, Me-25); signals for the sugar moiety, see Table 1. ^{13}C-NMR (C_5D_5N) δ: 38.9 (C-1), 26.6 (C-2), 88.2 (C-3), 39.6 (C-4), 56.0 (C-5), 18.5 (C-6), 33.1 (C-7), 39.7 (C-8), 48.0 (C-9), 37.0 (C-10), 23.8 (C-11), 122.5 (C-12), 145.0 (C-13), 42.1 (C-14), 28.4 (C-15), 23.8 (C-16), 47.1 (C-17), 41.4 (C-18), 41.2 (C-19), 36.6 (C-20), 29.1 (C-21), 32.7 (C-22), 28.1 (C-23), 17.0 (C-24), 15.6 (C-25), 17.4 (C-26), 26.2 (C-27), 180.2 (C-28), 73.9 (C-29), 19.8 (C-30); signals for the sugar moiety, see Table 1.

Acid Hydrolysis of 24 Compound **24** (7.5 mg) was subjected to acid hydrolysis as described for **10** to give 3β,29-dihydroxyolean-12-en-28-oic acid (2.6 mg) and a sugar fraction (3.1 mg). HPLC analysis of the sugar fraction under the same conditions as in the case of **10** resulted in identification of L-arabinose, D-glucose, and L-rhamnose.

Compound **25**: Amorphous solid, $[\alpha]_D^{28}$ +6.0° (c=0.10, MeOH). HR-ESI-TOF-MS (positive mode) m/z: 951.4980 $[M+Na]^+$ (Calcd for $C_{47}H_{76}O_{18}Na$: 951.4929). IR (film) ν_{max} cm^{-1}: 3383 (OH), 2932 (CH), 1687 (C=O), 1072. ^{1}H-NMR (C_5D_5N) δ: 6.23 (1H, br s, H-1″), 5.50 (1H, br s, H-12), 5.07 (1H, d, J=6.4 Hz, H-1′), 5.04 (1H, d, J=7.8 Hz, H-1‴), 4.28 (1H, dd, J=11.8, 4.4 Hz, H-3), 4.18 (1H, d, J=10.7 Hz, H-23a), 3.76 (1H, d, J=10.7 Hz, H-23b), 3.58 (2H, s, H_2-29), 3.41 (1H, dd, J=13.8, 4.1 Hz, H-18), 1.65 (3H, d, J=6.1 Hz, Me-6″), 1.24 (3H, s, Me-27), 1.21 (3H, s, Me-30), 1.09 (3H, s, Me-24), 1.03 (3H, s, Me-26), 0.93 (3H, s, Me-25). ^{13}C-NMR (C_5D_5N) δ: 39.0 (C-1), 26.3 (C-2), 80.6 (C-3), 43.5 (C-4), 47.8 (C-5), 18.1 (C-6), 32.8 (C-7), 39.7 (C-8), 48.2 (C-9), 36.9 (C-10), 23.8 (C-11), 122.6 (C-12), 144.9 (C-13), 42.1 (C-14), 28.4 (C-15), 23.7 (C-16), 47.1 (C-17), 41.3 (C-18), 41.2 (C-19), 36.6 (C-20), 29.1 (C-21), 32.7 (C-22), 63.9 (C-23), 14.0 (C-24), 16.1 (C-25), 17.4 (C-26), 26.1 (C-27), 180.2 (C-28), 73.8 (C-29), 19.7 (C-30), 104.3 (C-1′), 74.6 (C-2′), 83.2 (C-3′), 68.8 (C-4′), 65.6 (C-5′), 101.8 (C-1″), 72.4 (C-2″), 72.6 (C-3″), 74.0 (C-4″), 69.9 (C-5″), 18.6 (C-6″), 105.0 (C-1‴), 74.9 (C-2‴), 78.3 (C-3‴), 71.5 (C-4‴), 78.6 (C-5‴), 62.6 (C-6‴).

Acid Hydrolysis of 25 Compound **25** (9.4 mg) was subjected to acid hydrolysis as described for **10** to give 3β,23,29-trihydroxyolean-12-en-28-oic acid (3.0 mg) and a sugar fraction (4.4 mg). HPLC analysis of the sugar fraction under the same conditions as in the case of **10** resulted in identification of L-arabinose, D-glucose, and L-rhamnose.

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