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TERPENOIDS OF *RHODODENDRON JAPONICUM*

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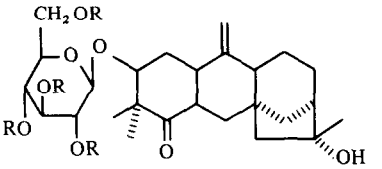
Key Word Index—*Rhododendron japonicum*; Ericaceae; diterpene glucoside; triterpene; pieroside B; grayanoside B; asiatic acid; 2α,3α,24-trihydroxyurs-12-en-28-oic acid; 2α,3α,19,24-tetrahydroxyurs-12-en-28-oic acid.

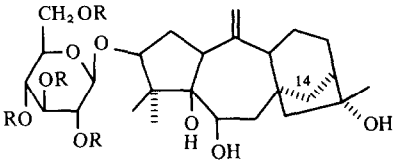
Abstract—From *Rhododendron japonicum* were isolated two diterpene glucosides, pieroside B and grayanoside B, and two new triterpenes, 2α,3α,24-trihydroxyurs-12-en-28-oic acid and 2α,3α,19,24-tetrahydroxyurs-12-en-28-oic acid, whose structures were established by chemical and spectroscopic means.

INTRODUCTION

In the course of our investigations of the Ericaceae family [1], we have now focused on *Rhododendron japonicum*, which is a poisonous shrub widely distributed throughout Japan, and from which seven toxic diterpenes named rhodojaponins were isolated by Hikino *et al.* [2]. We now wish to report the isolation and structure elucidation of two diterpene glycosides, a sugar and three triterpenes, two of which were new compounds, from the title plant.



1 R = H
1a R = Ac

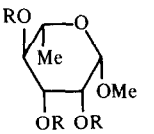


2 R = H
2a R = Ac

RESULTS AND DISCUSSION

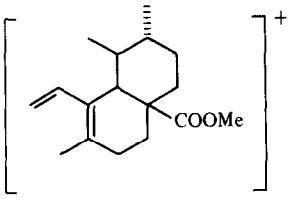
The methanol extract of twigs and leaves of *Rhododendron japonicum* was diluted with water and extracted with chloroform, ethyl acetate and *n*-butanol, successively. The *n*-butanol-soluble portion was fractionated by silica gel CC, and acetylated with acetic anhydride and pyridine, giving two acetates of diterpene glycosides. One of them was identified as tetraacetylpieroside B (**1a**) [1], and the other as pentaacetylgrayanoside B (**2a**) [3]. Compound **1** is the first leucothane derivative, and compound **2** is the first grayanane derivative with no hydroxyl group on C-14, isolated from this plant.

From the ethyl acetate-soluble portion was separated a sugar (**3**), which on acetylation gave a triacetate (**3a**), $C_{13}H_{20}O_8$. The physical and spectral data of **3a** were identical with those reported for methyl triacetyl-β-L-rhamnoside [4].

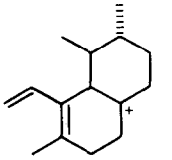


3 R = H
3a R = Ac

From the chloroform-soluble portion was obtained a mixture of triterpenes, which was treated with diazomethane and the products separated by silica gel prep. TLC, giving three compounds **4a**, **5a** and **6a**. The physical and chemical properties of **4a** and **5a** were very similar. Their molecular formulas were revealed to be $C_{31}H_{50}O_5$ by high resolution mass spectroscopy. On acetylation they gave triacetates **4b** and **5b**, whose IR spectra showed no hydroxyl absorption. Therefore their five oxygens could be attributed to one carboxyl and three hydroxyls, that is, $C_{29}H_{44}(OH)_3(COOMe)$. Considering that their ^1H NMR spectra showed one proton triplet on a trisubstituted double bond around δ 5.2, they should be pentacyclic triterpenes. Abundant ions in the mass spectra of **4a** and **5a** at *m/z* 262 and 203 correspond to ions *a* and *b*,

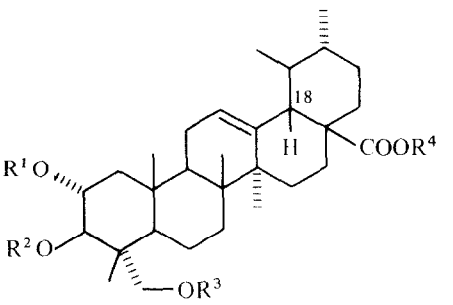


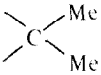
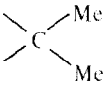
a : *m/z* 262

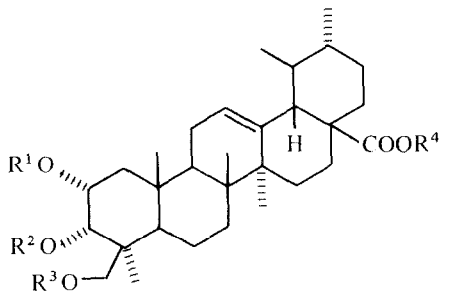


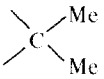
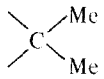
b : *m/z* 203

suggesting that fragmentation was occurring in a manner typical of urs-12-enes or olean-12-enes with a C-17 methoxycarbonyl and with no hydroxyl groups on rings



	R^1	R^2	R^3	R^4
4	H	H	H	H
4a	H	H	H	Me
4b	Ac	Ac	Ac	Me
4c	H			Me
4d	Ac			Me
4e	Ac	H	H	Me



	R^1	R^2	R^3	R^4
5	H	H	H	H
5a	H	H	H	Me
5b	Ac	Ac	Ac	Me
5c			H	Me
5d			Ac	Me
5e	H	H	Ac	Me

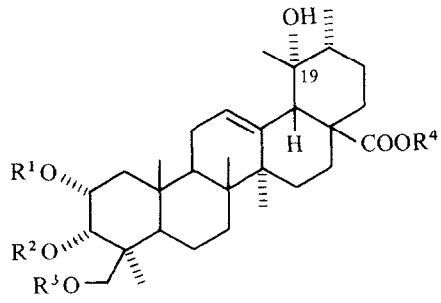
D/E [5]. The assignment of the carboxyl group to the C-17 position was supported by the CD curves of **4a** and **5a** (**4a** $[\theta]_{217}$-6705; **5a** $[\theta]_{218}$-7054) which were very similar to those of a series of Δ^{12}-triterpene-28-carboxylic acids [6]. The presence of a hydroxyl group on ring B was ruled out by the fact that both **4a** and **5a** formed the triacetate under mild conditions. In the ^{1}H NMR spectra of **4b** and **5b** the signal due to the C-18 proton appeared as a doublet (J = 10–12 Hz) around δ 2.25. Therefore compounds **4** and **5** should have the ursane skeleton [7]. The ^{1}H NMR spectra of **4b** and **5b** indicate the presence of one primary and two secondary acetoxyl groups (Table 1). Treatment of **4a** and **5a** with acetone and *p*-toluenesulfonic acid under mild conditions gave the isopropylidene derivatives **4c** and **5c**, respectively, which on acetylation and then hydrolysis by acid gave the monoacetates **4e** and **5e**. The ^{13}C NMR spectra of both **4e** and **5e** showed a signal due to C-13 at δ 138.2, which supported the conclusion that they had an ursane skeleton [8]. From the ^{1}H NMR spectra of these derivatives (**4a**–**4e** and **5a**–**5e**), the position of hydroxyl groups were revealed to be C-2, C-3 and C-4 in both compounds. The triterpenes having hydroxyl groups on such positions which are reported in the literature are asiatic acid (**7**) [9] and esculentic acid (**8**) [10]. Comparing the ^{1}H NMR spectra of the methyl ester triacetates of these compounds (Table 1), compound **4** was presumed to be asiatic acid and it was identical with the authentic sample.

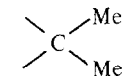
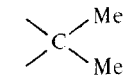
The coupling patterns of H-2 and H-3 in the ^{1}H NMR of **5b** (δ 5.32, *m*, $W_{1/2}$ = 21 Hz, H-2; δ 5.19, *d*, J = 3 Hz, H-3) indicated that H-2 was axial and H-3 equatorial thereby indicating that the C-2 and C-3 hydroxyl groups were α-equatorial and α-axial, respectively [7]. The appearance of two doublets at δ 4.06 and 4.20 (J = 12 Hz) indicated the axial nature of the C-4 acetoxymethylene group since an equatorial one resonates at higher field than δ 3.9 [11, 12]. Compound **5** thus can be assigned as 2α,3α,24-trihydroxyurs-12-en-28-oic acid.

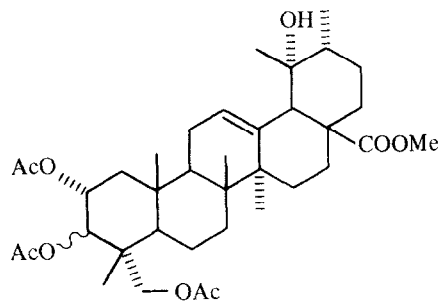
Compound **6a** had the molecular formula $C_{31}H_{50}O_6$ as determined by high resolution mass spectroscopy. On mild acetylation it gave a triacetate **6b**, whose IR spectrum still showed hydroxyl absorption at 3525 cm^{-1}, and the ^{1}H NMR spectrum indicated the presence of one primary and two secondary acetoxyl groups (Table 1). In the mass spectrum of **6a**, the ions at *m/z* 278, 260, 201 and 179 corresponded with the fragmentation observed with urs-12-enes or olean-12-enes having a carbomethoxy group at C-17 and a hydroxyl group on rings D/E [5, 13]. The ^{1}H NMR spectrum of **6b** showed one proton singlet at δ 2.60 for H-18, suggesting that the hydroxyl group in rings D/E was placed at the C-19 position [13]. Therefore the other three hydroxyls must be situated in ring A. Treatment of **6a** with acetone and *p*-toluenesulfonic acid followed by acetylation and acid hydrolysis afforded an isopropylidene derivative **6c** and a monoacetate **6e** as in the case of compound **5**. The chemical shift (δ 138.1) due to C-13 in the ^{13}C NMR spectrum of **6e** indicated that **6** had an ursane skeleton. From the ^{1}H NMR spectra of

Table 1. ^{1}H NMR Chemical Shifts (δ) of Methyl Acetylurs-12-en-28-oates ($CDCl_3$)

	4b	**5b**	**6b**	**7**	**8**	**9**	**10**
–Me	0.76, 0.89	0.74, 0.98	0.68, 0.98	0.76, 1.25	—	0.70, 0.97	0.70, 0.99
	1.08, 1.11	1.05, 1.12	1.05, 1.22,	0.87–1.11		1.10, 1.20	1.08, 1.12
			1.32			1.30	1.20, 1.31
–COMe	2.00, 2.04	1.96, 2.09	1.97, 2.10	1.90, 1.94	1.90, 1.93	1.93, 1.98	1.95, 1.99
	2.10	2.16	2.14	2.00	2.00	2.02	2.05
H-18	2.25	2.26	2.63	—	—	2.60	2.60
	(*d*, J = 10 Hz)	(*d*, J = 12 Hz)	(*s*)			(*s*)	(*s*)
–COOMe	3.62	3.61	3.62	3.54	—	3.60	3.58
$-CH_2OAc$	3.59, 3.88	4.05, 4.20	4.06, 4.21	3.59, 3.75	3.42–3.75	3.90	3.88
	(*d*, J = 12 Hz)	(*d*, J = 12 Hz)	(*d*, J = 12 Hz)	(*d*, J = 12 Hz)	(*dd*, J = 10 Hz)	(2H)	(2H, *q*)
H-2	5.17	5.19	5.20				5.26
	(*dd*, J = 10, 4Hz)	(*m*, $W_{1/2}$ = 21 Hz)	(*m*, $W_{1/2}$ = 18 Hz)		4.85–5.02	5.12	(*m*, $W_{1/2}$ = 9 Hz)
				4.70–5.40	(2H, *m*,$W_{1/2}$ = 18 Hz)	(2H)	
H-3	5.09	5.32	5.34	(3H, complex)			5.18
	(*d*, J = 10 Hz)	(*d*, J = 3 Hz)	(*d*, J = 3 Hz)				(*d*, $W_{1/2}$ = 3.5 Hz)
H-12	5.28	5.26	5.38		5.28	5.32	5.35
	(*t*, J = 3 Hz)	(*t*, J = 4 Hz)	(*t*, J = 3 Hz)		(*br s*)	(*s*)	(*m*)



	R^1	R^2	R^3	R^4
6	H	H	H	H
6a	H	H	H	Me
6b	Ac	Ac	Ac	Me
6c			H	Me
6d			Ac	Me
6e	H	H	Ac	Me



7	3β-OAc	R = H	(= **4b**)
8	3α-OAc	R = H	
9	3β-OAc	R = OH	
10	3α-OAc	R = OH	

these derivatives, compound **6** should have hydroxyls on C-2, C-3 and C-4 as in compound **5**. Such triterpenes found in nature are 23-hydroxytormentic acid (**9**) [13] and 2α,3α,19,23-tetrahydroxyurs-12-en-28-oic acid (**10**) [14]. By comparing the ^{1}H NMR spectra of these compounds (Table 1), the structure of **6** was confirmed as 2α,3α,19,24-tetrahydroxyurs-12-en-28-oic acid.

EXPERIMENTAL

All mps are uncorr. IR spectra were recorded on KBr discs. The ^{1}H NMR spectra were run at 200 and 100 MHz and the ^{13}C NMR spectra at 50 and 25 MHz with TMS as internal standard. Mass spectra (70 eV) were taken with a direct inlet.

Plant Material. Leaves and stems of *Rhododendron japonicum* Suringer (20 kg) were collected at Nagano prefecture, Japan, in 1980.

Extraction and isolation. The powdered leaves and stems of *R. japonicum* were extracted under reflux with MeOH. The extracts were diluted with H_2O and extracted at room temp. with $CHCl_3$, EtOAc and *n*-BuOH, successively. The $CHCl_3$ extract was defatted with hexane. The hexane-insoluble portion was chromatographed on a silica gel column. The triterpenoid containing fraction was obtained from the $CHCl_3$–MeOH (97:3) eluate. Chlorophyll was removed by passing through a silanized silica gel column using MeOH–H_2O (1:1) as eluent. The triterpenoid mixture thus obtained was methylated with CH_2N_2 to yield a product which showed three spots (**4a**, **5a** and **6a**) on TLC, which were separated by silica gel prep. TLC using $CHCl_3$–MeOH (9:1) as solvent.

The EtOAc extract was chromatographed on a silica gel column. From the $CHCl_3$–MeOH (24:1) eluate was obtained a sugar fraction, which was acetylated with Ac_2O and C_5H_5N to give **3a**.

The *n*-BuOH extract was fractionated on a silica gel column. A part of the $CHCl_3$–MeOH (93:7) eluate was purified by prep. TLC (solvent $CHCl_3$–MeOH, 4:1) and acetylated by Ac_2O and C_5H_5N to afford **1a**. The $CHCl_3$–MeOH (9:1) eluate gave crude **2**, which was purified on acetylation with Ac_2O and C_5H_5N to afford **2a**.

Tetraacetylpieroside B (**1a**). Mp 260° (decomp) (MeOH). Identified with the authentic sample from *Pieris japonica* [1].

Pentaacetylgrayanoside B (**2a**). Mp 209–211° (*i*-PrOH). Identified with the authentic sample from *P. japonica* [1]. ^{1}H NMR ($CDCl_3$): δ 0.96, 1.04, 1.38 (each 3H, *s*), 2.00, 2.02, 2.03, 2.05, 2.07 (each 3H, *s*), 4.20 (2H, *m*), 4.52 (1H, *d*, J = 8 Hz), 4.88–5.40 (many protons).

Methyl triacetyl-β-L-rhamnoside (**3**). Colorless needles, mp 154–156°. (Found: C, 51.10; H, 7.09. Calc. for $C_{13}H_{20}O_8$: C, 51.31; H, 6.63%). IR ν_{max} cm^{-1}: 1745, 1370, 1225, 1055. ^{1}H NMR ($CDCl_3$): δ 1.30 (3H, *d*, J = 6.2 Hz), 2.05, 2.11, 2.18 (each 3H, *s*), 3.52 (3H, *s*), 3.52 (1H, *m*, H-5), 4.52 (1H, *d*, J = 1 Hz, H-1), 5.01 (1H, *m*, H-3), 5.06 (1H, *m*, H-4), 5.46 (1H, *dd*, J = 1 and 2.8 Hz, H-2). ^{13}C NMR ($CDCl_3$): δ 170.5 (*s*), 170.1 (*s*), 169.8 (s), 99.5 (*d*, C-1),

71.2 (*d*, C-4), 70.8 (*d*, C-3), 70.6 (*d*, C-5), 69.0 (*d*, C-2), 57.3 (*q*, OMe), 20.9 (*q*), 20.8 (*q*), 20.6 (*q*), 17.4 (*q*, C-6). The ^{13}C NMR signals were assigned by means of single frequency off-resonance decoupling and selective proton decoupling.

Methyl asiatate (**4a**). Recrystallization from MeOH afforded fine crystals, mp 222–223°, $[\alpha]_D^{21}$ + 55.08° (*c* 2.62, $CHCl_3$). IR ν_{max} cm^{-1}: 3420–3340, 1725. ^{1}H NMR ($CDCl_3$): δ 0.78, 0.96, 1.01, 1.10 (each 3H, *s*), 2.23 (1H, *d*, *J* = 10 Hz, H-18), 3.59 (3H, *s*, OMe), 3.4–3.8 (4H, *m*), 5.23 (1H, *m*, H-12). MS: *m/z* 502.3652 (M^+, calc. for $C_{31}H_{50}O_5$, 502.3658), 484, 466, 442, 262, 203 (base peak), 133.

Methyl triacetylasiatate (**4b**). To 50 mg of **4a** were added C_5H_5N (1 ml) and Ac_2O (1 ml). The reaction mixture was kept at room temp. overnight, poured into H_2O, and extracted with Et_2O. The Et_2O extract was purified by prep. TLC (solvent: C_6H_6–EtOAc, 17:3) to give 58 mg of **4b**, amorphous. IR ν_{max} cm^{-1}: 1740, 1240. MS: *m/z* 628.3971 (M^+, calc. for $C_{37}H_{56}O_8$, 628.3974), 568 [M^+ − AcOH], 508 [M^+ − 2AcOH], 262 (base peak), 203, 133.

Methyl 3,23-O-*isopropylideneasiatate* (**4c**). To an Me_2CO soln (5 ml) of **4a** (50 mg) was added 50 mg of TsOH. The reaction mixture was kept at room temp. overnight, poured into H_2O, neutralized with 5% K_2CO_3 and then extracted with EtOAc. The EtOAc layer was purified by prep. TLC (solvent: C_6H_6–EtOAc, 6:4) to give 33 mg of **4c**, amorphous. IR ν_{max} cm^{-1}: 3475, 1725. ^{1}H NMR ($CDCl_3$): δ 0.74, 1.04, 1.08, 1.10, 1.46, 1.46 (each 3H, *s*), 2.24 (1H, *d*, *J* = 12 Hz, H-18), 3.32 (1H, *d*, *J* = 10 Hz, H-3), 3.50 (2H, *s*, –CH_2O–), 3.60 (3H, *s*, OMe), 3.60 (1H, *m*, H-2), 5.26 (1H, *m*, H-12).

Acetate of **4c** (**4d**). Compound **4c** (50 mg) was acetylated with Ac_2O and C_5H_5N to give 45 mg of **4d**, colorless crystals, mp 241° (decomp) (MeOH). (Found: C, 74.10; H, 9.67. Calc. for $C_{36}H_{56}O_6$: C, 73.93; H, 9.65%.) ^{1}H NMR ($CDCl_3$): δ 0.73, 1.09, 1.12, 1.40, 1.42 (each 3H, *s*), 2.00 (3H, *s*, Ac), 2.23 (1H, *d*, *J* = 10 Hz, H-18), 3.50 (2H, *s*, –CH_2O–), 3.54 (1H, *d*, *J* = 10 Hz, H-3), 3.59 (3H, *s*, OMe), 5.00 (1H, *dt*, *J* = 4 and 10 Hz, H-2), 5.24 (1H, *m*, H-12).

Methyl 2-*acetylasiatate* (**4e**). To an MeOH soln (3 ml) of **4d** (50 mg) was added TsOH (20 mg) and the mixture refluxed for 3 min. The reaction mixture was poured into H_2O, neutralized with 5% K_2CO_3, and then extracted with EtOAc. The EtOAc extract was purified by prep. TLC (solvent: $CHCl_3$–MeOH, 9:1) to afford 41 mg of **4e**, amorphous. IR ν_{max} cm^{-1}: 3430, 1725, 1240. ^{1}H NMR ($CDCl_3$): δ 0.75, 0.85, 0.95, 1.08 (each 3H, *s*), 2.06 (3H, *s*, Ac), 2.23 (1H, *d*, *J* = 10 Hz, H-18), 3.36 (1H, *d*, *J* = 10 Hz, H-3), 3.60 (3H, *s*, OMe), 3.63 (2H, –CH_2O–), 5.03 (1H, *dt*, *J* = 3 and 10 Hz, H-2), 5.24 (1H, *m*, H-12). ^{13}C NMR ($CDCl_3$): δ 178.0 (C-28), 171.5 (*s*, Ac), 138.2 (C-13), 125.1 (C-12), 76.5 (C-3), 72.9 (C-2), 68.2 (C-23), 52.8 (C-18), 51.4 (*q*, OMe), 48.0 (C-17), 48.0 (C-5), 47.5 (C-9), 43.7 (C-1), 43.1 (C-4), 42.1 (C-14), 39.5 (C-8), 39.0 (C-19), 38.8 (C-20), 38.1 (C-10), 36.6 (C-22), 32.6 (C-7), 30.7 (C-21), 28.0 (C-15), 24.2 (C-16), 23.6 (C-27), 23.4 (C-11), 21.3 (*q*, Ac), 21.1 (C-30), 18.1 (C-6), 17.0 (C-25), 17.0 (C-26), 17.0 (C-29), 12.9 (C-24).

The procedure for derivative formation of compounds **5** and **6** was the same as in the case of compound **4**.

Methyl 2α,3α,24-*trihydroxyurs*-12-*en*-28-*oate* (**5a**). Amorphous powder, $[\alpha]_D^{21}$ + 49.97° (*c* 2.47, MeOH), IR ν_{max} cm^{-1}: 3415, 1722. ^{1}H NMR ($CDCl_3$): δ 0.69, 0.91, 0.93, 1.08 (each 3H, *s*), 2.22 (1H, *d*, *J* = 10 Hz), 3.27 (1H, *d*, *J* = 10 Hz), 3.59 (3H, *s*), 3.73–3.96 (3H), 5.20 (1H, *m*). MS: *m/z* 502.3646 [M]$^+$, calc. for $C_{31}H_{50}O_5$, 502.3658, 484 [M − H_2O]$^+$, 466 [M − 2H_2O]$^+$, 262, 203 (base peak).

Triacetate of **5a** (**5b**). Amorphous. IR ν_{max} cm^{-1}: 1740, 1240. MS: *m/z* 628.3956 [M]$^+$, calc. for $C_{37}H_{56}O_8$, 628.3974, 568 [M − AcOH]$^+$, 508 [M − 2AcOH]$^+$, 262, 203 (base peak), 133, 43.

Isopropylidene derivative of **5a** (**5c**). IR ν_{max} cm^{-1}: 3475, 1722. ^{1}H NMR ($CDCl_3$): δ 0.71, 0.86, 1.09, 1.18, 1.24, 1.50 (each 3H, *s*), 2.13 (1H, *d*, *J* = 10 Hz), 3.59 (3H, *s*), 3.59 (2H), 4.16 (2H, *m*), 5.25 (1H, *m*).

Acetate of **5c** (**5d**). IR ν_{max} cm^{-1}: 1735, 1725, 1235. ^{1}H NMR ($CDCl_3$): δ 0.72, 0.90, 0.90, 1.16, 1.34, 1.50 (each 3H, *s*), 1.12 (3H, *d*, *J* = 7 Hz), 2.06 (3H, *s*), 3.59 (3H, *s*), 3.96 (1H, *d*, *J* = 5 Hz), 4.03 (2H, *s*), 4.23 (1H, *dd*, *J* = 5 and 11 Hz), 5.25 (1H, *m*).

24-*Monoacetate of* **5a** (**5e**). Colorless needles, mp 202–204° (EtOAc). (Found: C, 72.31; H, 9.43. Calc. for $C_{33}H_{52}O_6$: C, 72.75; H, 9.62%). IR ν_{max} cm^{-1}: 3440, 1725, 1715, 1245. ^{1}H NMR ($CDCl_3$): δ 0.72, 0.97, 1.09, 1.12 (each 3H, *s*), 0.93 (3H, *d*, *J* = 7 Hz), 2.04 (3H, *s*), 2.22 (1H, *d*, *J* = 11 Hz), 3.58 (3H, *s*), 3.67 (1H, *d*, *J* = 3 Hz), 3.87, 4.17 (each 1H, *d*, *J* = 11 Hz), 4.0 (1H, *m*), 5.22 (1H, *br s*). ^{13}C NMR ($CDCl_3$): δ 178.0 (C-28), 171.2 (*s*, Ac), 138.2 (C-13), 125.1 (C-12), 73.6 (C-3), 67.0 (C-24), 66.1 (C-2), 52.8 (C-18), 51.4 (*q*, OMe), 48.5 (C-5), 48.0 (C-17), 47.4 (C-9), 42.3 (C-4), 42.1 (C-14), 41.6 (C-1), 39.6 (C-8), 39.0 (C-19), 38.8 (C-20), 38.0 (C-10), 36.6 (C-22), 33.0 (C-7), 30.7 (C-21), 28.0 (C-15), 24.2 (C-16), 23.7 (C-27), 23.4 (C-11), 22.6 (C-23), 21.1 (*q*, Ac), 20.9 (C-30), 18.2 (C-6), 17.0 (C-25), 16.8 (C-26), 16.8 (C-29).

Methyl 2α,3α,19,24-*tetrahydroxyurs*-12-*en*-28-*oate* (**6a**). Amorphous powder, $[\alpha]_D^{21}$ + 14.13° (*c* 2.94, MeOH). IR ν_{max} cm^{-1}: 3400, 1710. ^{1}H NMR (C_5D_5N): δ 0.84, 1.05, 1.34, 1.54, 1.58 (each 3H, *s*), 2.76 (1H, *s*), 3.68 (3H, *s*), 3.73, 4.09 (each 1H, *d*, *J* = 11 Hz), 4.40 (2H, *m*), 5.43 (1H, *m*).

Triacetate of **6a** (**6b**). Amorphous. IR ν_{max} cm^{-1}: 3525, 1738, 1240. MS: *m/z* 644.3933 [M]$^+$, calc. for $C_{37}H_{56}O_9$, 644.3924, 626 [M − H_2O]$^+$, 584 [M − AcOH]$^+$, 278, 260, 247, 201, 137, 179, 146, 133, 43 (base peak).

Isopropylidene derivative of **6a** (**6c**). Amorphous. IR ν_{max} cm^{-1}: 3475, 1720, 1040. ^{1}H NMR ($CDCl_3$): δ 0.64, 0.84, 0.95, 1.17, 1.20, 1.26, 1.33, 1.47 (each 3H, *s*), 2.66 (1H, *s*), 3.55 (3H, *s*), 3.55 (2H, *br s*), 4.11 (2H, *m*, $W_{1/2}$ = 8 Hz), 5.29 (1H, *m*).

Acetate of **6c** (**6d**). Amorphous. IR ν_{max} cm^{-1}: 3525, 1735, 1725, 1240. ^{1}H NMR ($CDCl_3$): δ 0.65, 0.87, 0.95, 1.14, 1.25, 1.31, 1.47 (each 3H, *s*), 2.56 (1H, *s*), 3.54 (3H, *s*), 3.96 (2H, *s*), 3.96 (2H, *m*), 5.28 (1H, *m*).

24-*Monoacetate of* **6d** (**6e**). Amorphous. IR ν_{max} cm^{-1}: 3490, 1735, 1720, 1235. ^{1}H NMR ($CDCl_3$): δ 0.66, 0.97, 1.13, 1.22, 1.27 (each 3H, *s*), 2.05 (3H, *s*), 2.60 (1H, *s*), 3.60 (3H, *s*), 3.60 (1H, *m*), 3.70 (1H, *d*, *J* = 3 Hz), 3.91, 4.20 (each 1H, *d*, *J* = 11 Hz), 5.38 (1H, *m*). ^{13}C NMR ($CDCl_3$): δ 178.3 (C-28), 171.2 (*s*, Ac), 138.1 (C-13), 128.6 (C-12), 73.6 (C-3), 73.0 (C-19), 67.1 (C-24), 66.0 (C-2), 53.2 (C-18), 51.6 (OMe), 48.4 (C-5), 47.9 (C-7), 47.0 (C-9), 45.5 (C-1), 42.3 (C-4), 41.4 (C-20), 41.2 (C-14), 40.0 (C-8), 38.0 (C-10), 37.4 (C-22), 32.8 (C-7), 28.0 (C-15), 27.3 (C-29), 26.0 (C-21), 25.4 (C-16), 24.5 (C-27), 23.8 (C-11), 22.6 (C-23), 20.9 (*q*, Ac), 18.3 (C-6), 16.6 (C-26), 16.5 (C-25), 16.1 (C-30).

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