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STEROIDAL SAPONINS, PARDARINOSIDE A–G FROM THE BULBS OF *LILIUM PARDARINUM*

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Key Word Index—*Lilium pardarinum*; Liliaceae; steroidal saponins; furostanol glycosides; spirostanol glycoside; pardarinoside A–G; bitter principles; bulbs.

Abstract—Novel steroidal saponins, pardarinoside A–G have been isolated as the bitter ingredients from the fresh bulbs of *Lilium pardarinum*. Their structures have been determined by high field NMR techniques and a few chemical transformations to be 22-*O*-methyl-26-*O*-acetyl-(25*R*)-5α-furost-3β,14α,17α,22α,26-pentaol 3-*O*-[α-L-rhamnopyranosyl(1→2)]-β-D-glucopyranoside, 22-*O*-methyl-26-*O*-acetyl-(25*R*)-5α-furost-3β,17α,22α,26-tetraol 3-*O*-[α-L-rhamnopyranosyl(1→2)]-β-D-glucopyranoside, 22-*O*-methyl-26-*O*-acetyl-(25*R*)-5α-furost-3β,14α,17α,22α,26-pentaol 3-*O*-[α-L-rhamnopyranosyl (1→2)] [β-D-glucopyranosyl (1→4)]-β-D-glucopyranoside, 22-*O*-methyl-26-*O*-acetyl-(25*R*)-5α-furost-3β,17α,22α,26-tetraol 3-*O*-[α-L-rhamnopyranosyl (1→2)] [β-D-glucopyranosyl (1→4)]-β-D-glucopyranoside, (25*R*)-5α-spirost-3β,17α,21-triol 3-*O*-[α-L-rhamnopyranosyl (1→2)] [α-L-arabinopyranosyl(1→3)]-β-D-glucopyranoside, 22-*O*-methyl-26-*O*-acetyl-(25*R*)-5α-furost-3β,14α,17α,22α,26-pentaol 3-*O*-[α-L-rhamnopyranosyl (1→2)] [α-L-arabinopyranosyl(1→3)]-β-D-glucopyranoside, and 22-*O*-methyl-26-*O*-acetyl-(25*R*)-5α-furost-3β,17α,22α,26-tetraol 3-*O*-[α-L-rhamnopyranosyl (1→2)]-[α-L-arabinopyranosyl(1→3)]-β-D-glucopyranoside. This is believed to be the first report of steriodal saponins from a *Lilium* species.

INTRODUCTION

Lilium plants (Liliaceae) are well known as garden plants and the bulbs have been used in medicine. In traditional Chinese medicine, they have been reputed to have a sedative, an antitussive, a nutrient or an anti-inflammatory activity [1, 2]. Our recent extensive studies on the chemical constituents of lily bulbs have shown the presence of a range of phenylpropanoid derivatives [3–8], an antitumour alkaloid and its glucoside [7, 9], and a cholestane glucoside [6].

Liliaceae plants are rich sources of steroidal saponins [10, 11]. There have been few reports on the steroidal sapogenins from the *Lilium* species [12, 13], but no publication can be traced concerning the steroidal saponins. The present paper provides a full account of the isolation and structure elucidation of seven steroidal saponins, for which we propose the names pardarinoside A (**1**), B (**2**), C (**3**), D (**4**), E (**5**), F (**6**), and G (**7**), from the fresh bulbs of *Lilium pardarinum* which is native to North America where it grows in damp places [14]. The structure assignments of the saponins which have new aglycone structures have been based upon extensive spectral analysis and chemical transformations. A part of this work has been reported in a preliminary communication [15].

RESULTS AND DISCUSSION

The methanolic bulb extract of *Lilium pardarinum* was partitioned between water and chloroform. The chloroform soluble fraction, upon repeated silica gel and Sephadex LH-20 column chromatography gave pure compounds **1**–**7**.

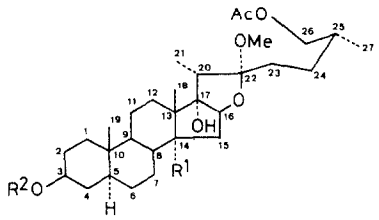
Pardarinoside A (**1**) was obtained as a white amorphous powder and exhibited a bitter taste. It formed a soapy lather when shaken with water and gave a positive coloration in the Liebermann–Burchard reaction. The IR spectrum showed the characteristic absorptions due to hydroxyl group (s) (3420 cm^{-1}) and a carbonyl group (1720 cm^{-1}). The ^1H and ^{13}C NMR spectra showed **1** to possess an acetyl group (δ2.05, 3H, *s*; δ170.8 and 20.8). On acid hydrolysis with 1 M hydrochloric acid, compound **1** liberated glucose and rhamnose, together with unidentified artifactual sapogenols which seemed to be derived from the genuine aglycone under the acidic conditions. The ^1H NMR spectrum of **1** exhibited two anomeric protons at δ5.07 (*d*, $J=7.2$ Hz) and 6.37 (*br s*)* which were consistent with the configurations β for D-glucose and α for L-rhamnose. The sequence of the oligoside moiety was easily determined as α-L-rhamnopyranosyl (1→2)-β-D-glucopyranoside, for which confirmatory evidence was inferred from the ^{13}C NMR spectrum [16]. The ^1H NMR spectrum showed signals for two tertiary methyl groups at δ1.09 (*s*, 18-Me) and 0.97 (*s*, 19-Me), two secondary methyl groups at δ1.34 (*d*, $J=7.1$ Hz, 21-Me) and 0.99 (*d*, $J=6.6$ Hz, 27-Me), and a methoxyl group at δ3.23 (*s*). The ^{13}C NMR spectrum gave a total of 27 carbons for the aglycone residue excluding a methoxyl carbon (δ47.2) and acetyl carbons (δ170.8 and 20.8). Thus, the structural feature of the aglycone moiety was deduced to be a 22-methoxyl furostanol derivative with

*In the previous communication [15], the signal at δ4.81 was assigned to the anomeric proton of the rhamnose in compound **1**. Detailed inspection of the 2D NOESY spectrum allowed us to revise the assignments; the signal at δ6.37 was reassigned to the the anomeric proton of the rhamnose and the signal at δ4.81 to the H-2 position of the rhamnose. In **1b**, **2** and **2b**, the assignments were also revised as described in the Experimental section.

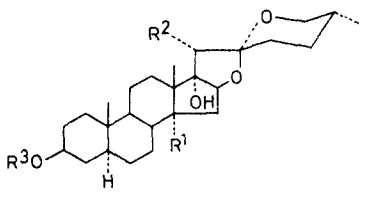
an acetyl group [17, 18]. Treatment of **1** with acetic anhydride in pyridine gave an acetyl derivative (**1a**) containing an additional six acetyl groups. The ^{13}C NMR chemical shifts of C-2, C-3, C-4, C-5 and C-19 in **1** were related to those of tigogenin 3-*O*-glycoside whose C-3 configuration was β and the relationship between the A and B rings was A/B *trans* [19]. In the ^{13}C NMR spectrum, two quaternary carbon signals bearing hydroxyl groups were observed (δ91.3 and 88.6), and the upfield shifts of the signals assignable to the C-7 (δ27.1), C-9 (δ46.6), C-12 (δ27.0) and C-21 (δ10.6), accompanied by a downfield shift of the signal due to the C-18 (δ21.0), compared with the signals of tigogenin 3-*O*-glycoside suggested the presence of 14α-and 17α-hydroxyl groups. The above result was further confirmed by the agreement of the ^{13}C NMR chemical shifts of the carbons of the D and E rings with those of ophiogenin [20], except for the C-22 position. A negative response of the Ehrlich reagent [21] and in the ^{1}H NMR spectrum a quartet signal (δ2.69, J = 7.1 Hz) arising from the H-20 methine proton also supported the presence of the C-17α hydroxyl group. Alkaline treatment followed by acid treatment of **1** yielded the corresponding spirostanol glycoside (**1b**). The acetyl group was concluded to be linked to the C-26 hydroxyl position as the signals at δ4.14 (*dd*, J = 10.8, 6.0 Hz) and 4.07 (*dd*, J = 10.8, 6.5 Hz) in **1** were replaced by the signal at δ3.52 (*br m*) in **1b**, assignable to the H-26 methylene protons in the ^{1}H NMR spectra. The C-25 configuration of **1b** was easily deduced to be *R* by the IR [22–24], ^{1}H, and ^{13}C NMR spectra [19]. The two dimensional NOE correlation spectroscopy (2D NOESY) spectrum of **1** made a significant contribution to the assignment of the C-22α configuration in which the cross peak was observed between the H-16α proton and the C-22 methoxyl protons. Thus, the structure of **1** was confirmed to be 22-*O*-methyl-26-*O*-acetyl-(25*R*)-5α-furost-3β,14α,17α,22α,26-pentaol 3-*O*-[α-L-rhamnopyranosyl (1 → 2)]-β-D-glucopyranoside.

Pardarinoside B (**2**) was a white amorphous powder. The spectral data of **1** and **2** were essentially analogous to one another. The ^{13}C NMR spectrum of **2** exhibited the resonance at δ90.4 of a quaternary carbon having a hydroxyl group. The appearence of a quartet signal due to the H-20 methine proton (δ2.55, J = 7.1 Hz), which coupled to only 21-Me protons in the ^{1}H NMR spectrum, suggested the occurrence of the C-17α hydroxyl group. In addition, the ^{13}C NMR chemical shifts of the carbons of the D and E rings were in good agreement with those of a nolonin-type glycoside [17], possessing a C-17α hydroxyl function. Acetylation of **2** with acetic anhydride in pyridine introduced six more acetyl groups (**2a**). By alkaline treatment followed by acid treatment of **2**, the C-26 acetyl substituent was cleaved and the side chain cyclized to give the corresponding spirostanol glycoside (**2b**) as in **1**. The C-25 configuration of **2b** was confirmed to be *R* by the IR, ^{1}H and ^{13}C NMR spectra. Accordingly, compound **2** was characterized as 22-*O*-methyl-26-*O*-acetyl-(25*R*)-5α-furost-3β,17α,22α,26-tetraol 3-*O*-[α-L-rhamnopyranosyl(1 → 2)]-β-D-glucopyranoside.

Pardarinoside C (**3**) was a more polar constituent than **1** and **2**. The signals of the aglycone moiety were superimposable on those of **1** in the ^{13}C NMR spectrum. The presence of one more terminal glucose was demonstrated by the appearence of the characteristic ^{13}C NMR signals (δ105.2, 78.4, 78.3, 74.9, 71.2 and 62.1). The ^{13}C NMR spectrum provided information for the establishment of the interglycosidic linkages [25]. The glycosidation shifts clearly showed the presence of 2,4-linked inner glucopyranoside, terminal rhamnopyranoside and terminal glucopyranoside, leading to the structure as Rha (1→2) [Glc (1→4)] Glc or Glc (1→2) [Rha (1→4)] Glc. The ^{1}H NMR spectrum of the acetyl derivative (**3a**) of **3** offered further support for the above findings. The H-2 and H-4 methine protons of the inner glucose moiety of **3a** appeared at δ3.85 and 3.54, respectively, whereas the other hydroxy methine and methylene protons appeared downfield as shown in Table 1. In the 2D NOESY spectrum of **3a**, the cross peak was observed between the anomeric proton of the rhamnose moiety and the H-2 proton of the inner glucose moiety [26]. On the basis of the facts referred to above, compound **3** was formulated as 22-*O*-methyl-26-*O*-acetyl-(25*R*)-5α-furost-3β,14α,17α,22α,26-pentaol 3-*O*-

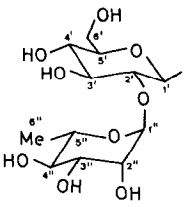


	R^1	R^2
1	OH	Rha — Glc —
2	H	Rha — Glc —
3	OH	Glc — Glc — (Rha)
4	H	Glc — Glc — (Rha)
6	OH	Ara — Glc — (Rha)
7	H	Ara — Glc — (Rha)

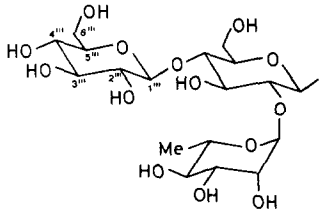


	R^1	R^2	R^3
1b	OH	Me	Rha — Glc —
2b	H	Me	Rha — Glc —
5	H	CH_2OH	Ara — Glc — (Rha)

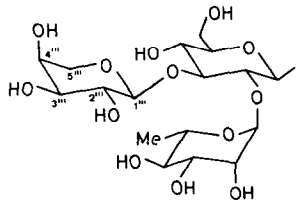
Rha — Glc- =



Glc — Glc-
|
Rha =



Ara — Glc-
|
Rha =



[α-L-rhamnopyranosyl (1→2)] [β-D-glucopyranosyl (1→4)]-β-D-glucopyranoside.

Pardarinoside D (**4**) had the same sapogenol skeleton as **2**, and the same oligoside constituent as **3**. The structure of **4** was established to be 22-*O*-methyl-26-*O*-acetyl-(25*R*)-5α-furost-3β,17α,22α,26-tetraol 3-*O*-[α-L-rhamnopyranosyl (1→2)] [β-D-glucopyranosyl (1→4)]-β-D-glucopyranoside.

Pardarinoside E (**5**) was a white amorphous powder. On TLC, compound **5** attracted attention because of a change in colour from yellow to bright fluorescent yellow after detection with 10% sulphuric acid and heating. The ^{13}C NMR spectrum showed three anomeric carbons at δ105.5, 102.5 and 99.5, and one secondary methyl carbon signal of rhamnose at δ18.7. The sugars obtained from the saponin hydrolysate were examined by TLC. The presence of glucose, rhamnose and arabinose was indicated by their R_f values and characteristic colours upon spraying the TLC plate with 10% sulphuric acid and heating. The anomeric configurations were readily recognized from the coupling constants of the ^{1}H NMR spectrum, β for D-glucose, α for L-rhamnose and α for L-arabinose. Application of the glycosidation shift rule of the ^{13}C NMR spectrum allowed easy recognition of the sugar sequence, 2,3-linked inner glucopyranoside, terminal rhamnopyranoside and terminal arabinopyranoside. In the ^{1}H NMR spectrum of the acetyl derivative (**5a**) of **5**, the hydroxy methine and methylene protons of the sugar moiety, except for the H-2 and H-3 protons of the inner glucopyranosyl moiety, were deshielded by the *O*-acetyl substitution to appear downfield. The correlation shown by the anomeric proton of the rhamnose moiety and the inner glucose H-2 proton in the 2D NOESY spectrum clarified that the oligoside structure was Rha (1→2) [Ara(1→3)] Glc. Lack of a methoxyl group, which is typical of the C-22 methoxyl furostanol derivatives and an acetyl group, as compared with the other saponins isolated together were the differences recognizable in spectroscopic data of **5**. The ^{1}H and ^{13}C NMR spectra of the aglycone moiety of **5** were analogous to those of **2a**, that is, 17α-hydroxy-(25*R*)-spirostanol glycoside. The ^{13}C NMR spectrum showed the existence of a hydroxy methylene group (δ59.1) and the ^{1}H NMR spectrum exhibited the presence of only a secondary methyl group (δ0.67, *d*, J=4.7 Hz, 27-Me). Furthermore, the multiplicity of the H-20 proton in the ^{1}H NMR spectrum was observed as the *dd* signal (δ2.67, J=8.6, 5.8 Hz). The above data accounted for the presence of the 21-methyleneoxy function. Thus, the unequivocal structure of **5** was proposed to be (25*R*)-spirost-3β,17α,21-triol 3-*O*-[α-L-rhamnopyranosyl (1→2)] [α-L-arabinopyranosyl (1→3)]-β-D-glucopyranoside.

Pardarinoside F (**6**) and G (**7**) were furostanol oligosides. The sugar moieties of **6** and **7** agreed with those of **5**, Rha (1→2) [Ara(1→3)] Glc. The structure of the aglycone moiety of **6** corresponded to that of **1**, and **7** to that of **2**. Pardarinoside F and G were determined to be 22-*O*-methyl-26-*O*-acetyl-(25*R*)-5α-furost-3β,14α,17α,22α,26-pentaol 3-*O*-[α-L-rhamnopyranosyl(1→2)] [α-L-arabinopyranosyl(1→3)]-β-D-glucopyranoside and 22-*O*-methyl-26-*O*-acetyl-(25*R*)-5α-furost-3β,17α,22α,26-tetarol 3-*O*-[α-L-rhamnopyranosyl(1→2)] [α-L-arabinopyranosyl(1→3)]-β-D-glucopyranoside, respectively.

Pardarinoside A–G are new naturally occurring steroidal saponins. The bitter taste of tomato seeds [27], peanut hearts (the embryo without the cotyledons) [28] and asparagus shoots [29] have been concluded to be due to the occurrence of steroidal saponins. Pardarinosides have a bitter taste and are considered to contribute the bitter taste of the bulbs of *L. pardarinum* as do the phenolic glycosides isolated previously [7]. Naturally occurring 22,26-hydroxyl furostanol saponins exist in the form of bisdesmoside, bearing sugars at both the C-3 and C-26 hydroxyl positions without any exceptions [19]. During partial hydrolysis of the sugar linkage to the C-26 hydroxyl position, they are readily cyclized to give the corresponding spirostanol glycosides [19]. Pardarinosides, except for pardarinoside E, are 22,26-hydroxyl furostanol derivatives, and it must be emphasized that they are distinctive in carring an acyl substitution in place of sugar to the C-26 hydroxyl position.

EXPERIMENTAL

^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz): TMS as int. standard. Assignments of the NMR spectra were accomplished on the basis of double resonance experiments, 2D NOESY and ^{13}C DEPT spectra, and by correlation with the data published for related compounds. CC: silica gel (Fuji Davison Co., Ltd BW-300 or BW-340) and Sephadex LH-20 (25–100 μm, Pharmacia Fine Chemicals Co., Ltd). TLC: precoated Kieselgel 60 F_{254} (0.25 mm thick, Merck).

Extraction and isolation. The dormant fresh bulbs of *Lilium pardarinum* (2.5 kg) purchased from Sakata-shubyo Co., Ltd, Kanagawa prefecture, Japan, were cut into pieces and extracted with hot MeOH. After removal of the solvent by evapn, the MeOH extract was suspended in H_2O and extracted with $CHCl_3$. The $CHCl_3$ extract was concd under red. pres., and sepd by repeated CC on silica gel with $CHCl_3$–MeOH, $CHCl_3$–MeOH–H_2O, Et_2O–MeOH–H_2O and EtOAc–MeOH–H_2O

Table 1. ^{1}H NMR spectral data for compounds **1a**, **2a**, **3a**, **4a**, **5a**, **6a**, and **7a**

	1a	**2a**	**3a**	**4a**	**5a**	**6a**	**7a**
3	3.68 *br m*	3.67 *br m*	3.71 *br m*	3.72 *br m*	3.73 *br m*	3.71 *br m*	3.73 *br m*
16	4.24 *t* $J=7.4$	3.90 *t* $J=7.6$	4.32 *t* $J=7.8$	4.00 *t* $J=7.6$	4.20 *t* $J=7.9$	4.30 $J=7.2$	4.00 t $J=7.4$
18, 19	0.95 *s*	0.82 *s*	0.88 *s*	0.85 *s*	0.92 *s*	0.88 *s*	0.86 ×2 *s*
	0.83 *s*	0.81 *s*	0.86 *s*	0.83 *s*	0.85 *s*	0.87 *s*	
20	2.38 *q* $J=7.1$	2.25 *q* $J=7.1$	2.40 *q* $J=7.1$	2.35 *q* $J=7.1$	2.45 *dd* $J=8.9$, 5.0	2.39 *q* $J=7.1$	2.34 *q* $J=7.1$
21	0.93 *d* $J=7.1$	0.91 *d* $J=7.1$	1.06 *d* $J=7.1$	1.09 *d* $J=7.1$	4.71 *dd* $J=11.4$, 8.9	1.04 *d* $J=7.1$	1.09 *d* $J=7.1$
					4.39 *dd* $J=11.4$, 5.0		
26	3.94 *dd* $J=10.8$, 6.2	3.94 *dd* $J=10.8$, 6.3	3.94 *dd* $J=10.9$, 6.0	3.94 *dd* $J=10.9$, 6.0	3.39 *br*	3.98–3.90 overlapping	3.94 *dd* $J=10.8$, 5.9
	3.87 *dd* $J=10.8$, 6.6	3.87 *dd* $J=10.8$, 6.7	3.89 *dd* $J=10.9$, 6.3	3.88 *dd* $J=10.9$, 6.5			3.88 *dd* $J=10.8$, 6.1
27	0.94 *d* $J=6.8$	0.94 *d* $J=6.7$	0.81 *d* $J=6.6$	0.81 *d* $J=6.7$	0.59 *d* $J=6.2$	0.81 *d* $J=6.6$	0.81 *d* $J=6.6$
OMe	3.21 *s*	3.20 *s*	3.03 *s*	3.04 *s*		3.01 *s*	3.04 *s*
Ac	2.12 *s*	2.12 *s*	1.91 *s*	1.91 *s*	1.90 *s*	1.90 *s*	1.90 *s*
	2.07 *s*	2.07 *s*	1.83 *s*	1.82 *s*	1.89 *s*	1.89 *s*	1.89 *s*
	2.05 ×2 *s*	2.06 *s*	1.73 *s*	1.73 *s*	1.83 *s*	1.84 *s*	1.83 *s*
	2.02 *s*	2.05 *s*	1.71 ×2 *s*	1.71 *s*	1.81 ×2 *s*	1.81 *s*	1.81 *s*
	2.00 *s*	2.02 *s*	1.69 *s*	1.70 *s*	1.75 *s*	1.80 *s*	1.80 *s*
	1.99 *s*	2.00 *s*	1.68 ×2 *s*	1.69 *s*	1.74 ×2 *s*	1.74 *s*	1.73 ×2 *s*
		1.99 *s*	1.62 *s*	1.68 ×2 *s*	1.61 *s*	1.73 *s*	1.70 *s*
				1.62 *s*		1.70 *s*	1.60 *s*
						1.59 *s*	

1′	4.58 *d* $J = 7.8$	4.58 *d* $J = 7.8$	4.29 *d* $J = 7.7$	4.30 *d* $J = 7.8$	4.33 *d* $J = 7.7$	4.30 *d* $J = 7.6$	4.32 *d* $J = 7.6$
2′	3.71 *dd* $J = 9.5, 7.8$	3.71 *dd* $J = 9.5, 7.8$	3.85 *dd* $J = 9.5, 7.7$	3.86 *dd* $J = 9.4, 7.8$	3.87 *dd* $J = 9.6, 7.7$	3.87 *dd* $J = 9.4, 7.6$	3.87 *dd* $J = 9.7, 7.6$
3′	5.23 *dd* $J = 9.5, 9.5$	5.23 *dd* $J = 9.5, 9.5$	5.54 *dd* $J = 9.5, 9.5$	5.54 *dd* $J = 9.4, 9.4$	3.95 *dd* $J = 9.6, 9.6$	3.98–3.90 overlapping	3.94 *dd* $J = 9.7, 9.7$
4′	4.95 *dd* $J = 9.5, 9.5$	4.95 *dd* $J = 9.5, 9.5$	3.54 *dd* $J = 9.5, 9.5$	3.55 *dd* $J = 9.4, 9.4$	5.17 *dd* $J = 9.6, 9.6$	5.17 *dd* $J = 9.4, 9.4$	5.17 *dd* $J = 9.7, 9.7$
5	3.68 *m*	3.67 *m*	3.23 *m*	3.21 *m*	3.43 *m*	3.43 *m*	3.43 *m*
6′	4.27 *dd* $J = 12.2, 5.1$	4.27 *dd* $J = 12.2, 5.0$	4.38 *dd* $J = 12.6, 4.1$	4.38 *dd* $J = 12.5, 4.1$	4.39 *dd* $J = 11.6, 4.8$	4.39 *dd* $J = 12.1, 4.6$	4.39 *dd* $J = 12.2, 4.7$
	4.08 *dd* $J = 12.2, 2.2$	4.08 *dd* $J = 12.2, 2.4$	3.87 *dd* $J = 12.6, 2.1$	3.87 *dd* $J = 12.5, 1.9$	4.20 *dd* $J = 11.6, 2.6$	4.20 *dd* $J = 12.1, 2.3$	4.20 *dd* $J = 12.2, 1.5$
1″	4.96 *d* $J = 1.9$	4.96 *d* $J = 1.8$	5.44 *d* $J = 1.6$	5.44 *d* $J = 1.8$	5.60 *d* $J = 1.3$	5.60 *d* $J = 1.4$	5.61 *d* $J = 1.6$
2″	4.99 *dd* $J = 3.4, 1.9$	4.99 *dd* $J = 3.4, 1.8$	5.46 *dd* $J = 3.2, 1.6$	5.46 *dd* $J = 3.2, 1.8$	5.72 *dd* $J = 3.5, 1.3$	5.74 *dd* $J = 3.6, 1.4$	5.73 *dd* $J = 3.4, 1.6$
3″	5.26 *dd* $J = 10.0, 3.4$	5.26 *dd* $J = 10.0, 3.4$	5.86 *dd* $J = 10.0, 3.2$	5.85 *dd* $J = 10.0, 3.2$	5.80 *dd* $J = 10.1, 3.5$	5.81 *dd* $J = 10.1, 3.6$	5.80 *dd* $J = 10.2, 3.4$
4″	5.06 *dd* $J = 10.0, 10.0$	5.06 *dd* $J = 10.0, 10.0$	5.63 *dd* $J = 10.0, 10.0$	5.63 *dd* $J = 10.0, 10.0$	5.58 *dd* $J = 10.1, 10.1$	5.59 *dd* $J = 10.1, 10.1$	5.59 *dd* $J = 10.2, 10.2$
5″	4.40 *dq* $J = 10.0, 6.2$	4.40 *dq* $J = 10.0, 6.2$	4.81 *dq* $J = 10.0, 6.3$	4.81 *dq* $J = 10.0, 6.2$	4.78 *dq* $J = 10.1, 6.2$	4.79 *dq* $J = 10.1, 6.3$	4.79 *dq* $J = 10.2, 6.2$
6″	1.18 *d* $J = 6.2$	1.18 *d* $J = 6.2$	1.43 *d* $J = 6.3$	1.43 *d* $J = 6.2$	1.34 *d* $J = 6.2$	1.35 *d* $J = 6.3$	1.34 *d* $J = 6.2$
1‴			4.33 *d* $J = 8.0$	4.33 *d* $J = 7.8$	4.86 *d* $J = 6.2$	4.86 *d* $J = 6.2$	4.86 *d* $J = 6.3$
2‴			5.18 *dd* $J = 9.3, 8.0$	5.18 *dd* $J = 9.3, 7.8$	5.40 *dd* $J = 8.7, 6.2$	5.41 *dd* $J = 8.7, 6.2$	5.40 *dd* $J = 8.7, 6.3$
3‴			5.35 *dd* $J = 9.3, 9.3$	5.35 *dd* $J = 9.3, 9.3$	5.50 *dd* $J = 8.7, 3.5$	5.50 *dd* $J = 8.7, 3.5$	5.50 *dd* $J = 8.7, 3.4$
4‴			5.20 *dd* $J = 9.3, 9.3$	5.20 *dd* $J = 9.3, 9.3$	5.19 *br m*	5.19 *br m*	5.20 *br m*
5‴			3.23 *m*	3.21 *m*	3.64 *dd* $J = 12.7, 4.0$	3.63 *dd* $J = 12.8, 4.1$	3.36 *dd* $J = 12.6, 4.0$
					3.29 *dd* $J = 12.7, 1.6$	3.28 *br d* $J = 12.8$	3.28 *dd* $J = 12.6, 1.5$
6‴			4.57 *dd* $J = 11.8, 1.7$	4.57 *dd* $J = 12.0, 1.7$			
			4.19 *dd* $J = 11.8, 5.9$	4.19 *dd* $J = 12.0, 5.8$			

Spectra of **1a** and **2a** were measured in $CDCl_3$ and those of **3a**, **4a**, **5a**, **6a**, and **7a** in C_6D_6.
All assignments were confirmed by double resonance experiments.
J values were expressed in Hz.
Assignments are interchangeable between the H-6′ and H-6‴ in **3a** and **4a**.

Table 2. ^{13}C NMR spectral data for compounds **1**, **1b**, **2**, **2b**, **3**, **4**, **5**, **6** and **7**

C	1	1b	2	2b	3	4	5	6	7
1	37.6	37.6	37.3	37.3	37.5	37.3	37.3	37.5	37.3
2	30.0	30.0	29.9	30.0	29.9	29.9	29.8	29.9	29.9
3	77.0	76.9	77.0	77.0	77.2	77.3	76.7	76.6	76.7
4	34.5	34.5	34.4	34.5	34.4	34.5	34.2	34.2	34.2
5	44.6	44.5	44.6	44.6[a]	44.5	44.7	44.6	44.5	44.6
6	29.1	29.0[a]	29.0	29.0	29.0	29.0	29.1	29.1	29.1
7	27.1[a]	27.0	32.5[a]	32.5[b]	27.0[a]	32.5[a]	32.5[a]	27.0[a]	32.5[a]
8	39.8	39.8	35.9	35.9	39.7	36.0	35.9	39.7	36.0
9	46.6	46.8	54.3	54.3	46.8	54.3	54.3	46.8	54.3
10	36.1	36.1	35.8	36.0	36.1	35.8	36.1	36.1	35.8
11	20.4	20.4	21.1	21.2	20.3	21.1	21.0	20.3	21.1
12	27.0[a]	27.0	32.2[a]	32.3[b]	26.9[a]	32.3[a]	33.2[a]	26.9[a]	32.3[a]
13	48.9	48.5	45.7	45.4	48.8	45.8	45.8	48.8	45.8
14	88.6	88.7	52.7	52.8	88.6	52.8	52.7[b]	88.6	52.8
15	40.2	40.2	31.5[a]	31.7[b]	40.1	31.6[a]	31.7[a]	40.1	31.6[a]
16	90.9	90.7	90.3	90.1	90.8	90.4	89.4	90.9	90.4
17	91.3	90.9	90.4	90.1	91.3	90.4	90.9	91.3	90.4
18	21.0	21.0	17.3	17.4[c]	21.0	17.3	17.3[c]	21.0	17.3
19	12.3	12.4	12.4	12.5	12.3	12.5	12.5	12.3	12.5
20	43.6	45.2	43.0	44.8[a]	43.5	43.0	52.6[b]	43.5	43.0
21	10.6	9.8	10.4	9.7	10.6	10.4	59.1	10.6	10.4
22	113.0	109.5	113.2	109.8	112.9	113.2	109.1	112.9	113.2
23	30.9	32.2	30.5	32.1[b]	30.8	30.6	31.9[a]	30.9	30.6
24	28.0	28.9[a]	27.9	28.8	28.0	28.0	28.8	28.0	28.0
25	33.3	30.4	33.2	30.5	33.3	33.3	30.4	33.3	33.3
26	69.3	66.8	69.2	66.7	69.2	69.2	66.8	69.2	69.2
27	16.9	17.3	16.8	17.3[c]	16.8	16.8	17.1[c]	16.9	16.8
OMe	47.2	—	47.0	—	47.1	47.0	—	47.2	47.0
Ac	170.8	—	170.8	—	170.8	170.8	—	170.8	170.8
	20.8	—	20.8	—	20.8	20.8	—	20.8	20.8
1′	99.9	99.8	99.8	99.9	99.5	99.6	99.5	99.4	99.5
2′	79.7	79.7	79.6	79.6	77.6[b]	77.6[b]	78.0[d]	78.0[d]	78.0[b]
3′	78.2[b]	78.2[b]	78.1[b]	78.1[d]	76.2	76.2	88.1	88.1	88.0
4′	72.0	72.0	71.9	72.0	82.1	82.2	69.6[e]	69.6[c]	69.6[c]
5′	78.3[b]	78.3[b]	78.2[b]	78.3[d]	77.7[b]	77.7[b]	77.9[d]	77.9[b]	77.9[b]
6′	62.9	62.8	62.8	62.8	62.0[e]	62.0[e]	62.6	62.6	62.6
1″	102.2	102.1	102.1	101.9	101.9	101.9	102.5	102.5	102.5
2″	72.6	72.6	72.5	72.6	72.4	72.4	72.4[f]	72.4[d]	72.4[d]
3″	72.9	72.9	72.8	72.9	72.7	72.8	72.8	72.9	72.8
4″	74.2	74.1	74.1	74.0	74.1	74.1	74.1	74.1	74.1
5″	69.5	69.4	69.4	69.4	69.4	69.4	69.4[e]	69.4[c]	69.4[c]
6″	18.7	18.7	18.6	18.6	18.6	18.7	18.7	18.7	18.7
1‴					105.2	105.2	105.5	105.5	105.5
2‴					74.9	75.0	72.3[f]	72.3[d]	72.3[d]
3‴					78.3[d]	78.3[d]	74.5	74.5	74.5
4‴					71.2	71.3	69.6[e]	69.6[c]	69.6[c]
5‴					78.4[d]	78.5[d]	67.8	67.8	67.7
6‴					62.1[e]	62.1[e]	—	—	—

Spectra were measured in pyridine-d_5.

[a–d] Assignments with the same superscript may be reversed in each column.

solvent systems, and Sephadex LH-20 with MeOH as the eluent to provide compounds **1**–**7**.

Pardarinoside A (**1**). A white amorphous powder, $C_{42}H_{70}O_{16}$, 663 mg, $[\alpha]_D^{27}$ −56.4°(MeOH; *c* 0.50). Secondary ion mass spectrometry (SIMS), *m/z* :799 $[M-OMe]^+$, 780 $[M-MeOH-H_2O]^+$. IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 2920, 2850 (CH), 1720 (C=O), 1450, 1365, 1235, 1120, 1040, 980. ^{1}H NMR (C_5D_5N): δ6.37 (1H, *br s*, H-1″), 5.07 (1H, *d*, *J* = 7.2 Hz, H-1′), 4.98 (1H, *dq*, *J* = 9.5, 6.2 Hz, H-5″), 4.81 (1H, *br s*, H-2″), 4.72 (1H, *dd*, *J* = 7.4, 6.0 Hz, H-16), 4.61 (1H, *dd*, *J* = 9.3, 3.2 Hz, H-3″), 4.14 (1H, *dd*, *J* = 10.8, 6.0 Hz, H-26a), 4.07 (1H, *dd*, *J* = 10.8, 6.5 Hz, H-26b), 3.96 (2H, *br m*, H-3 and -5′), 3.23 (3H, *s*, OMe), 2.69 (1H, *q*, *J* = 7.1 Hz, H-20), 2.05 (3H, *s*, Ac), 1.78 (3H, *d*, *J* = 6.2 Hz, H-6″), 1.34 (3H, *d*, *J* = 7.1 Hz, H-21), 1.09 (3H, *s*, H-18), 0.99 (3H, *d*, *J* = 6.6 Hz, H-27), 0.97 (3H, *s*, H-19). ^{13}C NMR: Table 2.

Acid hydrolysis of **1**. Compound **1** (6.0 mg) was hydrolysed with 1 M HCl (H_2O–dioxane, 1:1) at 100° for 2 hr. The reaction mixture was examined by TLC with *n*-BuOH–Me_2CO–H_2O

(4:5:1) to detect glucose (R_f 0.30) and rhamnose (R_f 0.65), which were identical with authentic specimens. When developed with $CHCl_3$–MeOH solvent system, many spots due to artifactual sapogenols were detected on TLC.

Acetylation of **1**. Compound **1** (40.0 mg) was dissolved in Ac_2O and pyridine and the soln was kept at room temp. After addition of H_2O and removal of the solvent, the crude product was extracted with $CHCl_3$ and the $CHCl_3$ soln was subjected to CC on silica gel with *n*-hexane–Me_2CO (3:1) to give a pure acetate (**1a**), 30.9 mg. A white amorphous powder, $C_{54}H_{82}O_{22}$. IR ν_{max}^{KBr} cm^{-1}: 3470 (OH), 2940 (CH), 1750 (C=O), 1450, 1370, 1230, 1170, 1135, 1080, 1040, 980, 910, 800, 755, 700. ^1H NMR: Table 1.

Alkaline treatment followed by acid treatment of **1**. Compound **1** (50.0 mg) in 1.5% NaOMe in MeOH was kept at room temp. for 30 min. The reaction soln was passed through a cation exchange resin (Amberlite IR-120B) and the soln concd to give a residue. The crude product was further treated with 0.2 M HCl (H_2O–dioxane, 1:1) at 50° for 5 min. The reaction soln was evapd to dryness under red. pres., and the product chromatographed over silica gel using $CHCl_3$–MeOH–H_2O (120:20:1) to yield the corresponding spirostanol glucoside (**1b**), 19.9 mg. A white amorphous powder, $C_{39}H_{64}O_{14}$, $[\alpha]_D^{22}$ −52.8 (MeOH; *c* 1.00). SIMS, *m/z*: 779 $[M+Na]^+$, 739 $[M-OH]^+$, 721 $[M-OH-H_2O]^+$, 593 $[M-Rha+H]^+$, 575 $[M-Rha-OH]^+$, 557 $[M-Rha-OH-H_2O]^+$, 430 $[aglycone-H_2O]^+$, 413 $[aglycone-H_2O-OH]^+$, 395 $[aglycone-2H_2O-OH]^+$. IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 2930, 2865 (CH), 1450, 1370, 1300, 1260, 1120, 1040, 975, 915, 890, 860 (intensity 915 < 890, 25*R* spiroketal), 810, 805. ^1H NMR (C_5D_5N): δ6.37 (1H, *br s*, H-1″), 5.05 (1H, *d*, *J* = 7.4 Hz, H-1′), 4.96 (1H, *dq*, *J* = 9.5, 6.2 Hz, H-5″), 4.81 (2H, overlapping, H-2″ and -16), 4.60 (1H, *dd*, *J* = 9.2, 3.4 Hz, H-3″), 3.95 (2H, *br m*, H-3 and -5′), 3.52 (2H, *br m*, H-26), 2.40 (1H, *q*, *J* = 7.2 Hz, H-20), 1.76 (3H, *d*, *J* = 6.2 Hz, H-6″), 1.28 (3H, *d*, *J* = 7.2 Hz, H-21), 1.10 (3H, *s*, H-18 or -19), 0.95 (3H, *s*, H-18 or -19), 0.68 (3H, *d*, *J* = 5.9 Hz, H-27). ^{13}C NMR: Table 2.

Pardarinoside B (**2**). A white amorphous powder, $C_{42}H_{70}O_{15}$, 263 mg, $[\alpha]_D^{27}$ −62.0° (MeOH; *c* 0.50). SIMS, *m/z*: 783 $[M-OMe]^+$. IR ν_{max}^{KBr} cm^{-1}: 3440 (OH), 2940 (CH), 1720 (C=O), 1455, 1370, 1240, 1125, 1050, 980, 905, 810. ^1H NMR (C_5D_5N): δ6.37 (1H, *br s*, H-1″), 5.07 (1H, *d*, *J* = 7.2 Hz, H-1′), 4.94 (H-5″, overlapping with H_2O signal), 4.80 (1H, *br s*, H-2″), 4.61 (1H, *dd*, *J* = 9.4, 3.3 Hz, H-3″), 4.12 (1H, *dd*, *J* = 10.8, 6.1 Hz, H-26a), 4.05 (1H, *dd*, *J* = 10.8, 6.5 Hz, H-26b), 3.95 (2H, *br m*, H-3 and -5′), 3.21 (3H, *s*, OMe), 2.55 (1H, *q*, *J* = 7.1 Hz, H-20), 2.05 (3H, *s*, Ac), 1.77 (3H, *d*, *J* = 6.2 Hz, H-6″), 1.28 (3H, *d*, *J* = 7.1 Hz, H-21), 0.97 (3H, *d*, *J* = 6.7 Hz, H-27), 0.95 (3H, *s*, H-18 or -19), 0.91 (3H, *s*, H-18 or -19). ^{13}C NMR: Table 2.

Acetylation of **2**. Compound **2** (20.0 mg) was acetylated with Ac_2O in pyridine. The crude acetate was purified through a silica gel column with *n*-hexane–Me_2CO (2:1) to give a pure acetate (**2a**), 17.7 mg. A white amorphous powder, $C_{54}H_{80}O_{21}$. IR ν_{max}^{KBr} cm^{-1}: 3530 (OH), 2950 (CH), 1750 (C=O), 1455, 1365, 1240, 1175, 1140, 1080, 1040, 980, 900, 800, 750. ^1H NMR: Table 1.

Alkaline treatment followed by acid treatment of **2**. Compound **2** (45.0 mg) was converted to the corresponding spirostanol glycoside (**2b**) (21.9 mg) by the same procedure as in the case of **1**. A white amorphous powder, $C_{39}H_{64}O_{13}$, $[\alpha]_D^{22}$ −66.8° (MeOH; *c* 0.37). SIMS, *m/z*: 740 $[M]^+$, 723 $[M-OH]^+$, 577 $[M-Rha+H]^+$, 559 $[M-Rha-OH]^+$. IR ν_{max}^{KBr} cm^{-1}: 3380 (OH), 2930, 2870 (CH), 1450, 1375, 1300, 1240, 1130, 1045, 975, 915, 895, 860 (intensity 915 < 895, 25*R* spiroketal), 815. ^1H NMR (C_5D_5N): δ6.38 (1H, *d*, *J* = 1.3 Hz, H-1″), 5.07 (1H, *d*, *J* = 7.2 Hz, H-1′), 4.96 (1H, *dq*, *J* = 9.5, 6.2 Hz, H-5″), 4.81 (1H, *dd*, *J* = 3.4, 1.3 Hz, H-2″), 4.61 (1H, *dd*, *J* = 9.3, 3.4 Hz, H-3″), 4.45 (1H, *dd*, *J* = 7.2, 6.6 Hz, H-16), 3.97 (2H, *br m*, H-3 and -5′), 3.51 (2H, *br d*, *J* = 7.0 Hz, H-26), 2.27 (1H, *q*, *J* = 7.2 Hz, H-20), 1.77 (3H, *d*, *J* = 6.2 Hz, H-6″), 1.23 (3H, *d*, *J* = 7.2 Hz, H-21), 0.96 (3H, *s*, H-18 or -19), 0.91 (3H, *s*, H-18 or -19), 0.69 (3H, *d*, *J* = 5.5 Hz, H-27). ^{13}C NMR: Table 2.

Pardarinoside C (**3**). A white amorphous powder, $C_{48}H_{82}O_{21}$, 302 mg, $[\alpha]_D^{22}$ −50.5° (MeOH; *c* 1.17). SIMS, *m/z*: 1016 $[M+Na-H]^+$, 961 $[M-MeOH-H]^+$, 519 $[aglycone-H]^+$. IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 2925 (CH), 1720 (C=O), 1450, 1365, 1240, 1050, 980, 900, 805. ^1H NMR (C_5D_5N): δ6.23 (1H, *br s*, H-1″), 5.12 (1H, *d*, *J* = 7.8 Hz, H-1′ or -1‴), 4.95 (1H, *d*, *J* = 7.2 Hz, H-1′ or -1‴), 4.91 (1H, *dq*, *J* = 9.4, 6.1 Hz, H-5″), 4.73 (1H, *br s*, H-2″), 4.72 (1H, *t*, *J* = 7.1 Hz, H-16), 4.55 (1H, *dd*, *J* = 9.3, 3.2 Hz, H-3″), 3.23 (3H, *s*, OMe), 2.68 (1H, *q*, *J* = 7.0 Hz, H-20), 2.06 (3H, *s*, Ac), 1.75 (3H, *d*, *J* = 6.1 Hz, H-6″), 1.33 (3H, *d*, *J* = 7.0 Hz, H-21), 1.08 (3H, *s*, H-18 or -19), 0.99 (3H, *d*, *J* = 6.5 Hz, H-27), 0.95 (3H, *s*, H-18 or -19). ^{13}C NMR: Table 2.

Acetylation of **3**. Compound **3** (25.0 mg) was acetylated with Ac_2O in pyridine. The crude product was chromatographed over silica gel using *n*-hexane–Me_2CO (2:1) to provide a pure acetate (**3a**), 13.8 mg. A white amorphous powder, $C_{66}H_{100}O_{30}$. IR ν_{max}^{KBr} cm^{-1} : 3490 (OH), 2940, 2871 (CH), 1752 (C=O), 1451, 1371, 1229, 1137, 1040, 983, 908, 837, 802. ^1H NMR: Table 1.

Pardarinoside D (**4**). A white amorphous powder, $C_{48}H_{82}O_{20}$, 77.6 mg $[\alpha]_D^{22}$ −59.7° (MeOH; *c* 0.79). SIMS, *m/z*: 945 $[M-MeOH-H]^+$, 503 $[aglycone-H]^+$. IR ν_{max}^{KBr} cm^{-1}: 3423 (OH), 2932, 2880 (CH), 1737, (C=O), 1456, 1377, 1310, 1260, 1246, 1061, 910, 813. ^1H NMR (C_5D_5N): δ6.23 (1H, *br s*, H-1″), 5.13 (1H, *d*, *J* = 7.8 Hz, H-1′ or -1‴), 4.95 (H-1′ or -1‴, overlapping with H_2O signal), 4.74 (1H, *br s*, H-2″), 3.22 (3H, *s*, OMe), 2.55 (1H, *q*, *J* = 7.0 Hz, H-20), 2.05 (3H, *s*, Ac), 1.75 (3H, *d*, *J* = 6.0 Hz, H-6″), 1.28 (3H, *d*, *J* = 7.0 Hz, H-21), 0.97 (3H, *d*, *J* = 6.7 Hz, H-27), 0.95 (3H, *s*, H-18 or -19), 0.90 (3H, *s*, H-18 or -19). ^{13}C NMR: Table 2.

Acetylation of **4**. A pyridine soln of **4** (30.0 mg) was treated with Ac_2O. The crude acetate was subjected to silica gel CC with *n*-hexane–EtOAc (1:1) and $CHCl_3$–EtOAc (3:1) to give a white amorphous powder (**4a**), 17.3 mg. $C_{66}H_{100}O_{29}$. IR ν_{max}^{KBr} cm^{-1}: 3531 (OH), 2953, 2880 (CH), 1752 (C=O), 1452, 1371, 1229, 1171, 1136, 1040, 983, 907, 838, 802. ^1H NMR: Table 1.

Pardarinoside E (**5**). A white amorphous powder, $C_{44}H_{74}O_{18}$, 125 mg, $[\alpha]_D^{22}$ −42.5° (MeOH; *c* 0.37). SIMS, *m/z*: 928 $[M+K-H]^+$, 449 $[aglycone+H]^+$, 431 $[aglycone-OH]^+$, 413 $[aglycone-OH-H_2O]^+$, 495 $[aglycone-OH-2H_2O]^+$, IR ν_{max}^{KBr} cm^{-1}: 3425 (OH), 2932, 2872 (CH), 1458, 1381, 1260, 1245, 1150, 1125, 1047, 980, 912, 868, 838, 812, 783. ^1H NMR (C_5D_5N): δ6.24 (1H, *br s*, H-1″), 4.98 (1H, *d*, *J* = 7.4 Hz, H-1′ or -1‴), 4.90 (1H, *d*, *J* = 7.5 Hz, H-1′ or -1‴), 4.87 (1H, *br s*, H-2″), 4.83 (1H, *dq*, *J* = 9.7, 6.1 Hz, H-5″), 4.62 (1H, *dd*, *J* = 7.4, 5.8 Hz, H-16), 4.54 (1H, *dd*, *J* = 9.4, 3.2 Hz, H-3″), 3.53 (2H, *br*, H-26), 2.67 (1H, *dd*, *J* = 8.6, 5.8 Hz, H-20), 1.72 (3H, *d*, *J* = 6.1 Hz, H-6″), 1.03 (3H, *s*, H-18 or -19), 0.88 (3H, *s*, H-18 or -19), 0.67 (3H, *d*, *J* = 4.7 Hz, H-27). ^{13}C NMR: Table 2.

Acid hydrolysis of **5**. A soln of **5** (100 mg) in 1 M HCl (H_2O–dioxane, 1:1) was refluxed at 100° for 2 hr. After solvent removal under red. pres., the crude mixture was subjected to silica gel CC using $CHCl_3$–MeOH–H_2O (2:1:0.5) and Sephadex LH-20 CC with MeOH as the eluent to give the sapogenol fraction and sugar fraction. The fractions were examined by TLC; the former with $CHCl_3$–MeOH (19:1) to detect many artifactual sapogenols, and the latter with *n*-BuOH–Me_2CO–H_2O (4:5:1) to detect glucose (R_f 0.31), arabinose (R_f 0.42) and rhamnose (R_f 0.64).

Acetylation of **5**. Compound **5** (30.0 mg) was acetylated with Ac_2O in pyridine. After usual work-up and chromatography on silica gel with *n*-hexane–Me_2CO (2:1) and *n*-hexane–EtOAc

(1:1), a pure acetate (**5a**) was obtained as a white amorphous powder, 25.5 mg, $C_{62}H_{92}O_{27}$. IR ν_{max}^{KBr} cm^{-1}: 3538 (OH), 2955, 2944, 2872 (CH), 1752 (C=O), 1456, 1371, 1225, 1175, 1160, 1136, 1090, 1050, 987, 920, 801. ^1H NMR: Table 1.

Pardarinoside F (**6**). A white amorphous powder, $C_{47}H_{80}O_{20}$, 71.6 mg, $[\alpha]_D^{22}$ −32.8° (MeOH; *c* 0.27). SIMS, *m/z*: 931 $[M-MeOH-H]^+$, 519 $[aglycone-H]^+$. IR ν_{max}^{KBr} cm^{-1}: 3435 (OH), 2936, 2874 (CH), 1724 (C=O), 1456, 1382, 1259, 1155, 1127, 1048, 1000, 940, 912, 868, 838, 812, 783. ^1H NMR (C_5D_5N): δ6.24 (1H, *br s*, H-1″), 4.99 (1H, *d*, *J* = 6.9 Hz, H-1′ or -1‴), 4.90 (1H, *d*, *J* = 7.7 Hz, H-1′ or -1‴), 4.87 (1H, *br s*, H-2″), 4.72 (1H, *t*, *J* = 6.5 Hz, H-16), 4.55 (1H, *dd*, *J* = 9.2, 3.0 Hz, H-3″), 3.23 (3H, *s*, OMe), 2.68 (1H, *q*, *J* = 7.0 Hz, H-20), 2.05 (3H, *s*, Ac), 1.73 (3H, *d*, *J* = 5.9 Hz, H-6″), 1.33 (3H, *d*, *J* = 7.0 Hz, H-21), 1.08 (3H, *s*, H-18 or -19), 0.99 (3H, *d*, *J* = 6.5 Hz, H-27), 0.96 (3H, *s*, H-18 or -19). ^{13}C NMR: Table 2.

Acetylation of **6**. Compound **6** (5.3 mg) was acetylated with Ac_2O in pyridine. After the usual work-up, the residue was purified by silica gel CC with *n*-hexane–Me_2CO (2:1) to give a pure acetate (**6a**), 1.9 mg. A white amorphous powder, $C_{63}H_{96}O_{28}$. IR ν_{max}^{KBr} cm^{-1}: 3476 (OH), 2962, 2940, 2866 (CH), 1752 (C=O), 1451, 1371, 1260, 1225, 1045, 802. ^1H NMR: Table 1.

Pardarinoside G (**7**). A white amorphous powder, $C_{47}H_{80}O_{19}$, 54.4 mg, $[\alpha]_D^{22}$ −40.8° (MeOH; *c* 0.39). SIMS, *m/z*: 915 $[M-MeOH-H]^+$, 503 $[aglycone-H]^+$. IR ν_{max}^{KBr} cm^{-1}: 3425 (OH), 2932 (CH), 1736 (C=O), 1456, 1378, 1246, 1150, 1135, 1050, 1000, 912, 865, 838, 814, 782. ^1H NMR (C_5D_5N): δ6.22 (1H, *br s*, H-1″), 4.98 (1H, *d*, *J* = 7.4 Hz, H-1′ or -1‴), 4.90 (1H, *d*, *J* = 7.5 Hz, H-1′ or −1‴), 4.44 (1H, *t*, *J* = 8.0 Hz, H-16), 4.87 (1H, *br s*, H-2″), 4.55 (1H, *dd*, *J* = 9.2, 3.1 Hz, H-3″), 3.21 (3H, *s*, OMe), 2.54 (1H, *q*, *J* = 7.0 Hz, H-20), 2.05 (3H, *s*, Ac), 1.72 (3H, *d*, *J* = 6.1 Hz, H-6″), 1.28 (3H, *d*, *J* = 7.0 Hz, H-21), 0.97 (3H, *d*, *J* = 6.7 Hz, H-27), 0.95 (3H, s, H-18 or -19), 0.90 (3H, *s*, H-18 or -19). ^{13}C NMR: Table 2.

Acetylation of **7**. Acetylation of **7** (20.0 mg) with Ac_2O in pyridine followed by CC over silica gel using *n*-hexane–Me_2CO (5:2) and *n*-hexane–EtOAc (1:1) gave a pure acetate (**7a**), 10.0 mg. A white amorphous powder, $C_{63}H_{96}O_{27}$. IR ν_{max}^{KBr} cm^{-1}: 3538 (OH), 2954 (CH), 1752 (C=O), 1455, 1371, 1225, 1172, 1136, 1055, 984, 909, 800. ^1H NMR: Table 1.

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