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HEDERAGENIN GLYCOSIDES FROM *POMETIA EXIMIA*

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Key Word Index—*Pometia eximia*; Sapindaceae; hederagenin; hederagenin glycosides; triterpene saponins.

Abstract—Seven new saponins, all glycosides of hederagenin (3β,23-dihydroxyolean-12-en-28-oic acid), were isolated from the stem of *Pometia eximia* along with hederagenin and two known saponins. Their structures were established as 28-*O*-β-D-apiosyl(1 → 2)-β-D-glucopyranosyl-, 3-*O*-α-L-arabinofuranosyl(1 → 3)[α-L-rhamnopyranosyl (1 → 2)]-β-D-xylopyranosyl-, 3-*O*-β-D-apiosyl(1 → 3)[α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranosyl-, 3-*O*-α-L-arabinofuranosyl(1 → 3)[α-L-rhamnopyranosyl-(1 → 2)]-β-L-arabinopyranosyl-, 3-*O*-β-D-xylopyranosyl(1 → 3)[α-L-rhamnopyranosyl(1 → 2)]-α-L-arabinopyranosyl-, 3-*O*-β-D-xylopyranosyl-(1 → 3)[α-L-rhamnopyranosyl(1 → 2)]-β-D-glucopyranosyl-, 3-*O*-β-D-galactopyranosyl(1 → 3)[α-L-rhamnopyranosyl(1 → 2)]-β-D-glucopyranosyl-hederagenins.

INTRODUCTION

The genus *Pometia* consists of *ca* 10 species distributed from Malaysia to India [1]. *Pometia eximia* is a tree of moderate size growing in Sri Lanka. No previous chemical work on this plant has been reported. The preliminary studies of a methanol extract of the stem of *P. eximia* showed a variety of biological activities, e.g. molluscicidal, larvicidal, antifungal and antibacterial activities. This prompted us to undertake phytochemical studies on this plant.

RESULTS AND DISCUSSION

The dry ground mature stem of *P. eximia* was defatted with petrol and then extracted with methanol. Separation of the methanol extract by chromatography on silica gel and reversed phase HPLC afforded hederagenin (**1**) [2] and nine hederagenin saponins, numbered **2**–**10** in order of increasing polarity. The structures of these saponins were elucidated by spectral methods including NOESY, H–H and C–H COSY NMR experiments, negative FAB-mass spectrometry (MS) and chemical hydrolysis. Acidic hydrolysis of the saponins commonly afforded hederagenin as an aglycone as well as component sugars, which were identified by GLC in the form of trimethylsilyl ethers.

Compound **2**, mp 215–217°, molecular formula $C_{35}H_{56}O_8$ [FABMS *m/z*: 603 $(M-H)^-$], and compound **3**, mp 258–260°, molecular formula $C_{40}H_{64}O_{12}$ [FABMS *m/z*: 735 $(M-H)^-$], were identified as 3-*O*-α-L-arabinopyranosyl and 3-*O*-β-D-xylopyranosyl(1 → 3)-α-L-arabinopyranosylhederagenins, respectively, on the basis of their spectral data. Compound **2** was previously isolated from *Caulophyllum robustum* [3], *Hedera helix* [4] and *Lonicera nigra* [5], while compound **3** was obtained from *Akebia quinata* [6].

Compound **4**, mp 222–224°, $[\alpha]_D^{25}$ − 7.4° (methanol; *c* 0.43), molecular formula $C_{41}H_{66}O_{13}$ [FABMS *m/z*: 765 $(M-H)^-$], was isolated as colourless microcrystals and afforded apiose and glucose upon acid hydrolysis. Fragment ion peaks at *m/z* 633 $[M-H-C_5H_8O_4]^-$ and 471 $[M-H-C_5H_8O_4-C_6H_{10}O_5]^-$ in the FAB mass spectrum indicated that apiose is the terminal sugar and glucose is the inner sugar. The remarkable intensity of the ion at *m/z* 471 (detected as the base ion peak) suggested that the sugar moiety was linked to hederagenin by an ester function [7]. This was established by the ^{13}C NMR spectrum of **4** (Table 1), which showed the signals of C-28 and C-3 of aglycone at δ178.1 and 74.0, respectively [8, 9]. The chemical shift of C-1 of glucose (δ94.7) further supported the 28-O-ester linkage [7, 9]. The ^1H NMR spectrum of **4** showed two anomeric proton signals assignable to H-1 of glucosyl moiety at δ5.38 (*d*, *J* = 7.3 Hz) and H-1 of apiosyl moiety at δ5.39 (*d*, *J* = 3.7 Hz) (Table 2). The H–H COSY spectrum showed the proton at δ5.38 was coupled to the signal at δ3.53 (H-2 of glucose, overlapped with H-3 of glucose) and this to the triplet signal at δ3.37 (H-4 of glucose). The H-4 signal was further coupled to the signal at δ3.30 (H-5 of glucose), which was in turn correlated with the signals at 3.66 and 3.79 (H-6 and 6′ of glucose). Similarly, it was possible to identify the coupling connectivities between the apiose anomeric proton and H-2 of apiose, and between H-4 and H-4′ of

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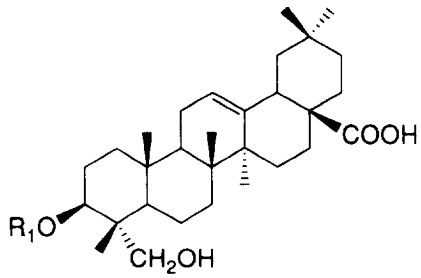
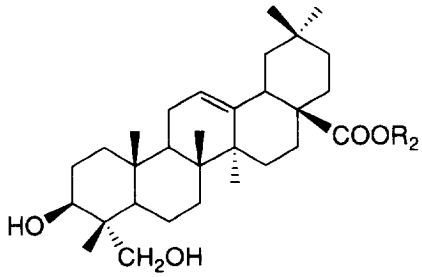


Cpd	R_1
1	H–
2	Ara–
3	Xyl^{3}–Ara–
5	Rha^{2}–Xyl– |3 Ara(*f*)
6	Rha^{2}–Glu– |3 Api
7	Rha^{2}–Ara*– |3 Ara(*f*)
8	Rha^{2}–Ara– |3 Xyl
9	Rha^{2}–Glu– |3 Xyl
10	Rha^{2}–Glu– |3 Gal



Cpd	R_2
4	Api^{2}–Glu–

Abbreviation: Api = β-D-apiofuranosyl, Ara(*f*) = α-L-arabinofuranosyl, Ara = α-L-arabinopyranosyl, Ara* = β-L-arabinopyranosyl, Gal = β-D-galactopyranosyl, Glu = β-D-glucopyranosyl, Rha = α-L-rhamnopyranosyl Xyl = β-D-xylopyranosyl.

apiose. The C–H COSY spectrum allowed assignment of the carbon signals attached to these protons. The signals for C-2 and C-3 of the glucosyl moiety were assigned as an interchangeable set due to the overlap of H-2 and H-3 of the moiety. A β-configuration of the anomeric centre of the glucosyl moiety was apparent from the magnitude of the coupling constant of H-1, while the configuration of the anomeric centre of the apiosyl moiety was determined as β, since the ^{13}C NMR data of this moiety were in good agreement with those of known β-apiosides [10, 11]. The glycosidation shift observed for C-2 [δ79.4 (or 78.6)] of the glucosyl moiety of **4** [reference ^{13}C data for a 28-*O*-β-D-glucopyranosyl ester [9]: δ95.9 (C-1), 73.9 (C-2), 78.2 (C-3), 71.1 (C-4), 78.3 (C-5), 62.4 (C-6)] indicated attachment of apiose at the C-2 position of the glucosyl moiety. The striking similarity between the ^{13}C NMR data for the sugar portion of **4** and those of the known saponins having a β-D-apiosyl(1 → 2)-β-D-glucopyranosyl unit [11] further supported the above structure assignment. Hence, the structure of **4** was established to be 28-*O*-β-D-apiosyl(1 → 2)-β-D-glucopyranosylhederagenin.

Compound **5**, mp 238–240°, $[\alpha]_D^{25}$ – 31.4° (methanol; *c* 0.29), molecular formula $C_{46}H_{74}O_{16}$ [*m/z*: 881 $(M-H)^-$] afforded rhamnose, xylose and arabinose upon acid hydrolysis. The ^{1}H NMR showed the presence of three anomeric signals at δ4.49 (*d*, *J* = 7.4 Hz), 5.08 (*br s*) and 5.05 (*d*, *J* = 1.8 Hz). The fragment ion peaks in the

Table 1. ^{13}C NMR data for compounds **1**–**10** (CD_3OD, 125 MHz)

Cpd	1	2	3	4	5	6	7	8	9	10
1	39.5	39.5	39.4	39.6	39.7	39.7	39.6	39.7	39.8	39.9
2	27.4	26.3	26.2	27.4	26.7	26.6	26.5	26.6	26.5	26.6
3	73.9	83.3	83.6	74.0	81.9	82.2	82.0	81.7	82.0	82.0
4	43.3	43.9	43.8	43.3	43.9	43.9	43.9	43.9	43.9	43.9
5	*	*	*	*	*	*	*	*	*	*
6	19.1	18.8	18.8	19.1	18.8	18.8	18.0	18.8	18.8	18.8
7	33.5	33.4	33.4	32.9	33.4	33.4	33.3	33.4	33.4	33.5
8	40.5	40.5	40.5	40.7	40.5	40.4	40.4	40.4	40.5	40.5
9	48.4	48.1	48.3	48.3	48.1	48.1	48.1	48.4	48.5	48.3
10	37.9	37.7	37.7	37.9	37.6	37.5	37.6	37.6	37.6	37.6
11	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.4	24.5
12	123.6	123.6	123.5	123.7	123.6	123.4	123.4	123.4	123.3	123.4
13	145.3	145.3	145.3	144.9	145.3	145.3	145.3	145.3	145.5	145.5
14	43.0	43.0	42.9	43.0	43.0	42.9	42.9	42.9	43.0	43.0
15	28.8	28.8	28.8	29.2	28.8	28.8	28.8	28.8	28.9	28.9
16	24.1	24.0	24.1	24.0	24.1	24.1	24.0	24.1	24.2	24.2
17	47.6	47.6	47.6	48.0	47.7	47.6	47.7	47.7	47.8	47.8
18	42.7	42.7	42.7	42.7	42.8	42.7	42.7	42.7	42.8	42.9
19	47.2	47.2	47.2	47.3	47.3	47.2	47.3	47.2	47.4	47.4
20	31.6	31.6	31.6	31.5	31.6	31.5	31.6	31.6	31.6	31.6
21	34.9	34.9	34.9	34.9	34.9	34.9	34.9	34.9	35.0	35.0
22	33.8	33.8	33.8	33.6	33.8	33.8	33.8	33.8	33.9	33.9
23	67.3	64.8	65.2	67.5	64.4	64.4	64.4	64.6	64.7	64.6
24	12.7	13.4	13.3	12.7	13.7	13.7	13.7	13.8	13.7	13.9
25	16.3	16.4	16.4	16.4	16.4	16.5	16.4	16.4	16.5	16.5
26	17.6	17.8	17.8	17.8	17.8	17.8	17.8	17.8	17.9	17.9
27	26.4	26.5	26.5	26.3	26.4	26.5	26.5	26.5	26.5	26.5
28	181.9	181.9	182.0	178.1	182.0	182.4	182.4	182.2	182.7	12.6
29	33.6	33.6	33.6	33.5	33.6	33.6	33.6	33.6	33.6	33.6
30	24.0	24.0	24.0	24.1	24.0	24.0	24.0	24.0	24.1	24.1
		Ara	Ara	Glu	Xyl	Glu	Ara	Ara	Glu	Glu
1		106.4	106.1	94.7	105.3	104.6	104.9	104.4	104.3	104.4
2		73.0	72.1	79.4†	78.6	78.4	75.7	75.1	78.1	78.2
3		74.5	83.7	78.6†	86.2	88.7	80.2	82.2	87.8	87.8
4		69.8	69.7	71.1	70.4	70.3	69.5	69.1	70.1	70.3
5		66.8	66.9	78.5	66.0	77.1	65.5	65.2	77.8	77.2
6				62.4		62.4			62.6	62.7†
			Xyl	Api	Rha	Rha	Rha	Rha	Rha	Rha
1			106.2	110.9	102.5	102.3	102.4	101.7	101.8	101.9
2			75.1	78.2	71.5	71.4	71.4	71.9	71.8	71.9
3			77.4	80.1	72.0	71.9	71.9	72.0	72.1	72.1
4			71.0	75.0	73.6	73.6	73.6	73.7	73.7	73.7
5			66.8	65.3	70.7	70.5	70.5	70.2	70.2	70.3
6					18.0	18.0	18.0	18.0	18.0	18.0
					Ara(*f*)	Api	Ara(*f*)	Xyl	Xyl	Gal
1					110.7	111.9	110.0	105.2	104.9	104.6
2					83.3	77.9	82.7	74.6	74.9	72.8
3					78.4	80.9	78.9	77.4	77.2	74.9
4					85.8	74.9	86.9	70.9	70.9	70.3
5					62.8	64.5	63.2	66.8	67.0	77.2
6										62.5†

*The signals were not clearly observed due to the overlap of the solvent signals.
†The assignments may be interchangeable.

FAB mass spectrum of **5** at *m/z* 749 $[M - H - C_5H_8O_4]^-$, 735 $[M - H - C_6H_{10}O_4]^-$, 603 $[M - H - C_5H_8O_4 - C_6H_{10}O_4]^-$ and 471 $[M - H - C_5H_8O_4 - C_6H_{10}O_4 - C_5H_8O_4]$ indicated that the sugar chain of **5** was branched. Careful analysis of the ^1H and ^{13}C NMR, H–H COSY and C–H COSY spectra of **5** gave evidence for the ring sizes of three sugar moieties and assigned the signals at δ102.5, 105.3 and 110.7 to

Table 2. ^{1}H NMR spectral data for compounds **1–10** (CD_3OD, 500 MHz)

Cpd	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
3	3.60 (*dd*, 11.8, 4.9)	3.60 (*dd*, 11.9, 5.5)	3.62*	3.59 (*dd*, 11.5, 5.1)	3.62 (*dd*, 12.5, 5.5)	3.68 (*dd*, 7.4, 3.7)	3.56*	3.63 (*dd*, 12.5, 5.0)	3.66*	3.68*
12	5.23 (*t*, 3.5)	5.23 (*t*, 3.5)	5.24 (*m*)	5.25 (*m*)	5.23 (*m*)	5.23 (*m*)	5.19 (*m*)	5.23 (*m*)	5.18 (*m*)	5.22 (*m*)
18	2.84 (*dd*, 13.7, 3.9)	2.84 (*dd*, 13.6, 3.8)	2.84 (*dd*, 13.8, 3.8)	2.80 (*dd*, 13.5, 3.7)	2.84 (*dd*, 13.9, 3.7)	2.85 (*dd*, 13.0, 3.7)	2.80 (*dd*, 11.0, 3.0)	2.85 (*dd*, 12.0, 3.8)	2.80 (*dd*, 11.0, 3.8)	2.84 (*dd*, 11.0, 3.7) 3.8)
23	3.29 (*d*, 10.8) 3.52 (*d*, 10.8)	3.29 (*d*, 12.0) 3.59 (*d*, 12.0)	3.30 (*d*, 10.1) 3.60 (*d*, 9.2)	3.29 (*d*, 12.9) 3.52 (*d*, 11.9)	3.30* 3.59 (*d*, 11.0)	3.31 (*d*, 10.1) 3.62 (*d*, 10.1)	3.28 (*d*, 12.4) 3.53 (*d*, 11.9)	3.32* 3.49 (*d*, 10.7)	3.30 (*d*, 11.0) 3.51 (*d*, 11.9)	3.35 (*d*, 11.0) 3.59 (*d*, 11.1)
24	0.69	0.70	0.71	0.70	0.69	0.71	0.65	0.67	0.67	0.71
25	0.97	0.97	0.97	0.97	0.96	0.96	0.91	0.95	0.92	0.96
26	0.81	0.81	0.81	0.80	0.80	0.81	0.77	0.80	0.78	0.81
27	1.16	1.17	1.17	1.12	1.17	1.17	1.12	1.17	1.12	1.16
29	0.90	0.90	0.90	0.90	0.90	0.90	0.86	0.88	0.85	0.89
30	0.93	0.93	0.94	0.93	0.94	0.93	0.89	0.92	0.89	0.93
		Ara	Ara	Glu	Xyl	Glu	Ara	Ara	Glu	Glu
1		4.31 (*d*, 6.5)	4.33 (*d*, 8.3)	5.38 (*d*, 7.3)	4.49 (*d*, 7.4)	4.55 (*d*, 8.3)	4.45 (*br s*)	4.51 (*d*, 7.1)	4.49 (*d*, 8.3)	4.53 (*d*, 7.4)
2		3.52*	3.68 (*t*, 8.7)	3.53*	3.38 (*t*, 9.2)	3.42 (*t*, 7.5)	3.67*	3.80*	3.50 (*t*, 8.2)	3.55 (*t*, 10.0)
3		3.48 (*dd*, 9.2, 3.7)	3.61*	3.53*	3.49 (*t*, 8.7)	3.51 (*t*, 8.3)	3.64*	3.77 (*dd*, 7.1, 3.6)	3.60 (*t*, 9.2)	3.67 (*t*, 8.3)
4		3.81 (*m*)	3.95 (*br s*)	3.37 (*t*, 9.2)	3.57*	3.41 (*t*, 8.8)	3.94 (*br s*)	3.95 (*br s*)	3.30*	3.48 (*t*, 9.2)
5		3.52*	3.55 (*d*, 11.9)	3.30*	3.22 (*dd*, 10.1, 11.9)	3.30 (*m*)	3.46 (*d*, 10.9)	3.49 (*d*, 10.7)	3.35 (*m*)	3.28 (*m*)
		3.82 (*dd*, 11.9, 2.8)	3.86 (*d*, 11.0)		3.88*		3.79 (*d*, 9.2)	3.82*		

Continued Overleaf

Table 2. *Continued*

Cpd	1	2	3	4	5	6	7	8	9	10
6				3.66 (*dd*, 11.9, 4.6)		3.69 (*d*, 11.8)			3.63*	3.68*
				3.79 (*dd*, 10.1, 1.0)		3.85 (*d*, 10.1)			3.79 (*dd*, 10.0, 1.0)	3.84 (*d*, 10.1)
			Xyl	Api	Rha	Rha	Rha	Rha	Rha	Rha
1			4.50 (*d*, 7.3)	5.39 (*d*, 3.7)	5.08 (*br s*)	5.17 (*br s*)	4.97 (*br s*)	5.21 (*br s*)	5.32 (*br s*)	5.38 (*br s*)
2			3.31 (*t*, 9.2)	3.92 (*d*, 3.7)	3.94 (*br s*)	3.98 (*br s*)	3.89 (*br s*)	3.92 (*br s*)	3.93 (*br s*)	3.98 (*br s*)
3			3.33 (*t*, 9.2)		3.71 (*dd*, 9.7, 3.7)	3.77 (*dd*, 9.6, 3.7)	3.68*	3.72 (*dd*, 10.7, 3.6)	3.69 (*dd*, 9.2, 3.7)	3.70*
4			3.51 (*td*, 9.0, 3.7)	3.98 (*d*, 10.1)	3.32 (*t*, 8.2)	3.41 (*t*, 8.8)	3.34 (*t*, 9.7)	3.38 (*t*, 10.7)	3.37 (*t*, 9.2)	3.39 (*t*, 9.6)
				3.72 (*d*, 9.2)						
5			3.20 (*t*, 10.6)	3.54 (*d*, 4.6)	3.86 (*m*)	3.81*	3.81*	3.83*	3.90 (*m*)	4.95 (*m*)
			3.85 (*t*, 11.0)							
6					1.23 (*d*, 6.4)	1.24 (*d*, 5.5)	1.20 (*d*, 6.5)	1.23 (*d*, 5.5)	1.18 (*d*, 6.4)	1.21 (*d*, 6.4)
					Ara (*f*)	Api	Ara(*f*)	Xyl	Xyl	Gal
1					5.05 (*d*, 1.8)	5.11 (*d*, 3.7)	5.06 (*br s*)	4.43 (*d*, 7.1)	4.40 (*d*, 7.3)	4.47 (*d*, 7.4)
2					4.07 (*t*, 6.4)	4.03 (*d*, 3.7)	4.04 (*br s*)	3.32*	3.28*	3.57*
3					3.88*		3.80*	3.32*	3.28*	3.50*
4					4.07 (*m*)*	4.15 (*d*, 10.0)				
5					3.60*	3.58 (*d*, 4.6)	3.59 (*d*, 11.9)	3.2 (*t*, 10.7)	3.22 (*t*, 9.2)	3.58*
					3.74 (*dd*, 12.8, 3.2)		3.66*	3.87*	3.89 (*t*, 11.0)	
6										3.68*
										3.84*

*Determined by C–H and H–H COSY spectra, although coupling constants could not be measured accurately due to the overlay of the signals.

anomeric carbons of rhamnopyranosyl, xylopyranosyl and arabinofuranosyl moieties, respectively. The configurations of the anomeric centres of arabinofuranosyl [δ5.05 (*d*, J = 1.8 Hz)] [12] and xylopyranosyl [δ4.49 (*d*, J = 7.4 Hz)] moieties were determined to be α and β respectively on the basis of the magnitude of the coupling constant of the anomeric protons. The configuration of the anomeric centre of the rhamnopyranosyl moiety was deduced as α from the coupling constant of the anomeric proton [δ5.08 (*br s*)] as well as the ^{13}C NMR data (Table 2) of the sugar moiety [13]. The NOESY spectrum of **5** showed the contour plots between H-3 of aglycone and H-1 of xylopyranosyl, H-2 of xylopyranosyl and H-1 of rhamnopyranosyl, and H-3 of xylopyranosyl and H-1 of arbinofuranosyl moieties. It was apparent from the chemical shifts of C-3 (δ81.9) and C-28 (δ182.0) that hederagenin was glycosidated at the 3-*O*-position [8]. Therefore, compound **5** was established to be 3-*O*-α-L-arabinofuranosyl-(1 → 3) [α-L-rhamnopyranosyl(1 → 2])-β-D-xylopyranosylhederagenin.

Compound **6**, mp 239–241°, $[\alpha]_D^{25}$ − 15.4° (methanol; *c* 0.51), molecular formula $C_{47}H_{76}O_{17}$ [*m/z* 911 $(M-H)^-$], afforded rhamnose, glucose and apiose upon acid hydrolysis. The FAB mass spectrum of **6** showed fragment ion peaks at *m/z* 779 $[M - H - C_5H_8O_4]^-$, 765 $[M - H - C_6H_{10}O_4]^-$, 633 $[M - H - C_6H_{10}O_4 - C_5H_8O_4]^-$ and 471 $[M - H - C_6H_{10}O_5 - C_6H_{10}O_4 - C_5H_8O_4]^-$. These fragment ions suggested a branched nature of the sugar chain and rhamnose and apiose being terminal sugars. Based on the H–H and C–H COSY data, the signals appeared at δ_H4.55 (*d*, J = 8.3 Hz)/δ_C104.6, 5.17 (*br s*)/102.3, and 5.11 (*d*, J = 3.7 Hz)/111.9 were assigned to those of the anomeric protons/carbons of β-glycopyranosyl, α-rhamnopyrano syl and β-apiosyl moieties, respectively. The configurations of the anomeric centres were assigned as described for compounds **4** and **5**. In the NOESY spectrum of **6** contour plots were observed between H-1 of glucosyl and H-3 of aglycone, H-2 of glucosyl and H-1 of rhamnosyl, H-3 of glucosyl and H-1 of apiosyl moieties, thus indicating the position of the glycosidic linkage. The downfield shift of C-2 and C-3 of the glucosyl moiety gave further evidence for the glycosylation of rhamnose at C-2 and apiose at C-3. Hence, the structure of **6** was established as 3-*O*-β-D-apiosyl(1 → 3)[α-L-rhamnopyranosyl(1 → 2)]-β-D-glucopyranosylhederagenin.

Compound **7**, mp 249–251°, $[\alpha]_D^{25}$ − 8.6° (methanol; *c* 0.97), molecular formula $C_{46}H_{74}O_{16}$ [FABMS *m/z* 881 $(M-H)^-$], was isolated as microcrystalline needles. Acid hydrolysis of **7** afforded arabinose and rhamnose. The FAB mass spectrum of **7** showed ion peaks at *m/z* 749 $[M - H - C_5H_8O_4]^-$, 735 $[M - H - C_6H_{10}O_4]^-$, 603 $[M - H - C_5H_8O_4 - C_6H_{10}O_4]^-$ and 471 $[M - H - C_5H_8O_4 - C_6H_{10}O_4 - C_5H_8O_4]^-$, suggesting the branched nature of the sugar chain and arabinose as the inner sugar. The C-3 and C-28 signals of the aglycone moiety of **7** appeared at δ82.0 and 182.4, respectively, thus indicating 3-*O*-glycoside [7]. The ^{1}H and ^{13}C NMR spectra and H–H and C–H COSY studies of **7** allowed assignment of H-1 and C-1 of β-arabinopyranosyl [δ_H4.45 (*br s*)/δ_C104.9], α-rhamnopyranosyl [4.97 (*br s*)/102.4] and α-arabinofuranosyl moiety [5.06 (*br s*)/110.6]. It should be noted that one arabinose moiety was present as arabinofuranose [12]. The NOESY spectrum of **7** gave evidence that rhamnopyranosyl and arabinofuranosyl moieties were linked to C-2 and C-3 of arabinopyranosyl, respectively. Hence, compound **7** was determined to be 3-*O*-α-L-arabinofuranosyl(1 → 3)[α-L-rhamnopyranosyl (1 → 2)-β-L-arabinopyranosyl hederagenin.

Compound **8**, mp 255–257°, $[\alpha]_D^{25}$ − 3.0° (methanol; *c* 0.25), molecular formula $C_{46}H_{74}O_{16}$ [FABMS *m/z*: 881 $(M-H)^-$], was isolated as microcrystals. Acid hydrolysis of **8** afforded arabinose, rhamnose and xylose. The FAB mass spectrum of **8** was identical to that of **7**. The chemical shifts of C-3 (δ81.7) and C-28(δ182.2) of the aglycone moiety of **8** indicated a 3-*O*-glycoside of hederagenin [7]. On the basis of H–H and C–H COSY data, the signals appeared at δ4.51 (*d*, J = 7.1 Hz)/104.4, 5.21 (*br s*/101.7, and 4.43 (*d*, J = 7.1 Hz)/105.2 were assigned to those of the anomeric protons/carbons of α-arabinopyranosyl, α-rhamnopyranosyl and β-xylopyranosyl moieties, respectively. Comparison of the ^{13}C NMR chemical shifts of the arabinopyranosyl moiety in **8** with those of **2** and **3** gave evidence for glycosilation linkages through C-2 and C-3. The NOESY spectrum of **8** established that rhamnose and xylose were attached to C-2 and C-3 of the arabinopyranosyl moiety, respectively. Thus, the structure of **8** was determined to be 3-*O*-β-D-xylopyranosyl-(1 → 3)[α-L-rhamnopyranosyl(1 → 2)]-α-L-arabinopyranosylhederagenin.

Compound **9**, mp 243–245°, $[\alpha]_D^{25}$ − 64.5° (methanol; *c* 0.1), molecular formula $C_{47}H_{76}O_{17}$ [FABMS *m/z*: 911 $(M-H)^-$], was isolated as microcrystals. Acid hydrolysis of **9** afforded glucose, rhamnose and xylose. The FAB mass spectrum of **9** showed ions peaks at *m/z* 779 $[M - H - C_5H_8O_4]^-$, 765 $[M - H - C_6H_{10}O_4]^-$, 633 $[M - H - C_5H_8O_4 - C_6H_{10}O_4]^-$ and 471 $[M - H - C_6H_{10}O_5 - C_6H_{10}O_4 - C_5H_8O_4]^-$, gave evidence for the branched nature of the sugar chain with the glucose as the inner sugar moiety. Based on the H–H and C–H COSY NMR data for **9** three anomeric proton/carbon signals at δ_H4.40 (J = 7.3 Hz)/δ_C104.9, 4.49 (J = 8.3 Hz)/104.3, 5.32 (*br s*)/101.8 were assigned to β-xylosyl, β-glucosyl and α-rhamnopyranosyl moieties, respectively. The downfield shift of C-2 and C-3 of the glucosyl moiety, compared to those of **6**, gave evidence for the glycosilation linkages through the C-2 and C-3 of the glucosyl moiety. It was shown from the NOESY spectrum of **9** that rhamnosyl and xylosyl moieties were linked to C-2 and C-3 of the glucosyl moiety, respectively. Hence, the structure of **9** was established as 3-*O*-β-D-xylopyranosyl(1 → 3)[α-L-rhamnopyranosyl(1 → 2)]-β-D-glucopyranosylhederagenin.

Compound **10**, mp 248–250°, $[\alpha]_D^{25}$ − 11.1° (methanol; *c* 0.31), molecular formula $C_{48}H_{78}O_{18}$ [FABMS *m/z*: 941 $(M-H)^-$], was isolated as microcrystals. Acid hydrolysis of **10** afforded glucose, rhamnose and galactose. The fragment ion peaks at *m/z* 795 $[M - H - C_6H_{10}O_4]^-$, 779 $[M - H - C_6H_{10}O_5]^-$, 633 $[M - H - C_6H_{10}O_4 -$

$C_6H_{10}O_5]^-$, 471 $[M - H - C_6H_{10}O_4 - C_6H_{10}O_5 - C_6H_{10}O_5]^-$, in the FAB mass spectrum of **10** suggested that the sugar chain was branched with a hexose unit as an inner sugar moiety. Based on the H–H and C–H COSY NMR data for **10** three anomeric proton/carbon signals at δ4.47 (*d*, J = 7.4 Hz)/104.6, 4.53 (*d*, J = 7.4 Hz)/104.4, 5.38 (*br s*)/101.9 were assigned to β-galactose, β-glucose and α-rhamnose moieties, respectively. Since the ^{13}C NMR chemical shifts of the glucosyl moiety of **9** and **10** are identical, it seemed highly likely that glucose was an inner sugar and it should be glycosylated at C-2 and C-3. The NOESY spectrum of **10** gave evidence that rhamnopyranosyl and galactopyranosyl moieties were linked to C-2 and C-3 of the glucosyl moiety, respectively. Thus, the structure of **10** was established as 3-*O*-β-D-galactopyranosyl(1 → 3)[α-L-rhamnopyranosyl (1 → 2)]-β-D-glucopyranosylhederagenin.

In conclusion, seven new glycosides of hederagenin, **4**–**10**, together with two known glycosides **2** and **3**, were isolated from *P. eximia*. These compounds were 3-*O*-glycosides of hederagenin, except compound **4**, which was linked to hederagenin by a C-28 ester function.

EXPERIMENTAL

Mps (uncorr.) were determined on a Yazawa BY-1 hot-stage microscope. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GSX-500 (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) spectrometer in CD_3OD soln with TMS as int. reference. Negative ion FAB mass spectra were obtained on a JEOL JMS-AX505HA spectrometer with glycerol as a matrix. CC was carried out on Kiesilgel 60 (70–230 mesh, Merck). HPLC was performed on a Shimadzu LC-6A apparatus equipped with a UV detector (206 nm) using a reversed-phase column (STR Prep-ODS from Shimadzu Techno Research, 25 cm × 20 mm i.d.). Typical conditions for HPLC were: solvent, CH_3CN–H_2O (4:5), and flow rate, 5 ml min^{-1}.

Extraction and isolation. The mature stem of *P. eximia* was collected from the central province of Sri Lanka in May, 1993. The plant was identified by Mr D. S. A. Wijesundara, Curator, Royal Botanical Gardens, Peradeniya, Sri Lanka. The dry ground stem of *P. eximia* (468 g) was sequentially extracted with hot petrol (40–60°) and hot MeOH. Evapn of the MeOH extract gave a dark-brown solid (58 g). A portion (20 g) was chromatographed over silica gel with $CHCl_3$ containing increasing amounts of 90% aq. MeOH, giving 8 frs: A (0.71 g, solvent ratio 99:1), B (0.20 g, 97.3), C (2.8 g, 19:1), D (0.41 g, 9:1), E (1 g, 8:2), F (1.2 g, 7:3), G (0.65 g, 3:2) and H (4.2 g, 0:100). Repeated CC of fr. A over silica gel gave **1** (18 mg, 0.011%). Similar sepn of fr. B followed by filtration through Sephadex LH-20 with MeOH as eluent afforded **2** (40 mg, 0.025%). Fr. C was further purified by CC over silica gel and HPLC to give **3** (800 mg, 0.50%). Similar separation of fr. D gave **4** (24 mg, 0.015%) and **5** (18 mg, 0.011%). HPLC purification of a portion of fr. E (400 mg) gave **6** (90 mg, 0.14%) and **7** (55 mg, 0.09%). Similar sepn of a portion of fr. F (400 mg) afforded **8** (55 mg, 0.10%) and **9** (95 mg, 0.18%). Repeated CC of fr. G over silica gel and HPLC (eluted with CH_3CN–H_2O, 2:3) gave **10** (40 mg, 0.025%). The most polar fr. H also contained several hederagenin glycosides, although we have not yet succeeded in obtaining pure materials.

Acid hydrolysis of compounds **2**–**10**. Each sample (*ca* 1 mg) was refluxed with 4 M HCl (200 μl) for 2 hr. The mixture was extracted with EtOAc. The organic layer was evapd to dryness to give **1**. The aq. phase was evapd to dryness, and the residue was dissolved in 20 μl trimethylsilylimidazole and gently warmed. This was diluted with 30 μl EtOAc, and a portion was analysed on Shimadzu GC-7A apparatus using a packed column (1% Shimalite W, 3 mm i.d. × 1 m) under a programmed temp.

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