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FURANOID DITERPENE GLUCOSIDES FROM *TINOSPORA RUMPHII*

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Key Word Index—*Tinospora rumphii*; Menispermaceae; furanoid diterpene glucosides; clerodane; rumphioside I.

Abstract—The stems of *Tinospora rumphii* yielded clerodane type furanoid diterpene glucosides: the new rumphioside I, the known borapetosides C and F and three other compounds. Their structures were established on the basis of various spectroscopic techniques. The three compounds have physical and spectral data identical to those of the reported compounds borapetosides E, D and B, respectively. However, the positions of the lactone rings of the first two compounds and the configuration of the bond attaching the glucose moiety to C-6 of the third differ from the reported ones.

INTRODUCTION

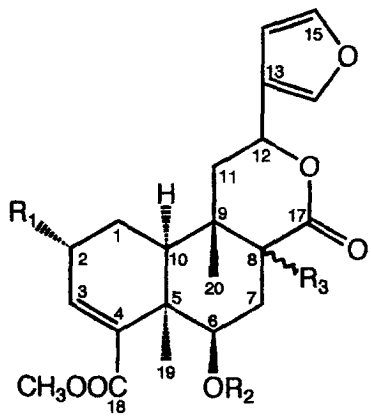
As part of our study of the constituents of *Tinospora rumphii* Boerl., a Philippine medicinal plant previously shown to have a significant stimulatory effect on glucose transport activity in mice [1], we reported earlier on the isolation and structure elucidation of seven new clerodane diterpene glucosides, rumphiosides A–F, from the stems of this plant [2]. Further chemical investigation of the same plant part resulted in the isolation of six additional clerodane diterpene glucosides. The structural identification of these compounds is discussed.

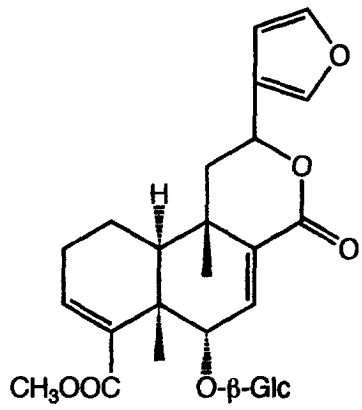
RESULTS AND DISCUSSION

The methanol extract of the dried ground stems of *T. rumphii* was successively partitioned against ether, 1-butanol and water. The butanol fraction was subjected to repeated silica gel and RP-18 column chromatography and preparative HPLC to give six compounds (**1**–**6**). The NMR spectra of these compounds suggested that they were all furanoid diterpene glucosides of the clerodane type.

Compounds **1** and **2** were identified as the known borapetosides C and F [3], respectively, based on their NMR spectral data and by a comparison of their spectral and physical properties with those reported in the literature for these two known diterpene glucosides.

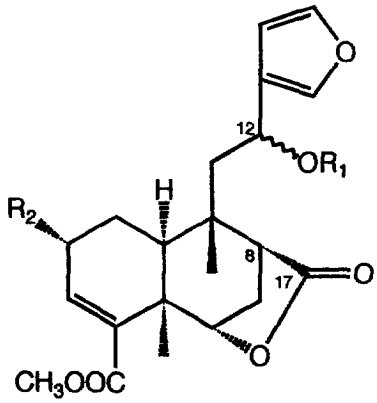
The ^{1}H and ^{13}C NMR spectra of **3**–**6**, which are summarized in Tables 1 and 2, suggested certain common structural features which are as follows: the presence of two angular methyl groups (C-19 and C-20), a methoxycarbonyl group (C-18), a furan ring (C-13 to C-16), and a trisubstituted double bond (C-3 and C-4). The spectra also showed signals attributable to one glucose moiety, except in the case of **4** which has two glucose moieties. In the ^{1}H NMR spectra, the coupling constants ($J = 7.6$–7.8 Hz) of the signals resulting from the anomeric protons of the glucopyranoses indicated the glycosidic linkages to have β-configurations. The ^{13}C NMR spectra, which were coupled with DEPT experiments, also showed signals attributable to two quaternary carbons (C-5 and C-9), two tertiary carbons (C-8 and C-10), three secondary carbons (C-1, C-7 and C-11), and two oxygenated methine groups (C-6 and C-12). From a biogenetic viewpoint, the events leading to the formation of the clerodane type bicyclic diterpenes produce the two angular methyls attached to C-5 and C-9 and the two ring junction methines at C-8 and C-10. Moreover, the methoxycarbonyl group is attached to C-4 [4]. The usefulness of the ^{13}C NMR chemical shifts of the angular methyls to distinguish between *cis* and *trans* A/B-ring junctions in clerodane diterpenes has been reported [5]. In the case of the *cis* clerodanes the C-19 methyl carbon atom resonates in a region lower than δ 20, and in the corresponding *trans* compounds it resonates in the region δ 11–19. The C-19 methyl signals of **3**–**6** were found at δ 26.8–29.3, thus, their A/B-ring junctions are *cis*. The mass fragmentation patterns of **3**–**6** showed peaks at *m/z* 81 which resulted from the cleavage of the C-11/C-12 bond and at *m/z* 94 which was due to cleavage along the C-9/C-11 and





2

1 $R_1 = H$; $R_2 = \beta$-Glc; $R_3 = \beta$-H
5 $R_1 = OH$; $R_2 = \beta$-Glc; $R_3 = \alpha$-H
8 $R_1 = OH$; $R_2 = H$; $R_3 = \alpha$-H



3 $R_1 = \beta$-Glc, $R_2 = H$
4 $R_1 = -\beta$-Glc-(6→1)-β-Glc, $R_2 = H$
6 $R_1 = \beta$-Glc, $R_2 = OH$
7 $R_1 = R_2 = H$

compounds involved other two-dimensional NMR analyses.

Compound **3** has the molecular formula $C_{27}H_{36}O_{11}$, as determined by high-resolution FAB-mass spectroscopy measured in the negative-ion mode. Enzymatic hydrolysis of **3** with crude hesperidinase yielded the aglycone, **7**.

The spectra of **7**, summarized in Tables 1 and 2, suggested the presence of all the common structural features of the isolated compounds mentioned above. Moreover, in its ^{13}C NMR spectrum, an additional triplet signal at δ 24.3 and a singlet signal at δ 178.0 which are attributable to a secondary carbon (C-2) and an ester carbonyl (C-17), respectively, were observed. The position of the C-17 ester carbonyl was established through an HMBC experiment which showed significant correlations between the signals corresponding to H-6 and C-17 and between H-8 and C-17 (Fig. 1). These correlations showed that the ester carbonyl is in were observed between the signals corresponding to (i) H-10 and Me-19, (ii) H-6 and Me-19, (iii) Me-20 and one of H-7 (δ 2.0), (iv) Me-20 and H-8 and (v) H-8 and H-12 (Fig. 1). From these results, it was deduced that H-10, Me-19 and the lactone ring are α-oriented, while Me-20, H-8 and H-12 are β-oriented.

In **3**, the glucose moiety was determined to be at C-12, as revealed by the downfield shift of the ^{13}C NMR signal of this carbon from δ 63.6 in **7** to δ 69.3 in **3** [6–7].

On the basis of these results, in conjunction with ^1H–^1H COSY and HSQC experiments, and from a comparison with the reported data of closely related compounds, the structure of **3** was identified as shown.

Compound **4** has the molecular formula $C_{33}H_{46}O_{16}$, based on its FAB mass spectrum. The ^1H and ^{13}C NMR spectra of **4** were identical to those of **3**, except for an additional glucose moiety. Its spectral data suggested the existence of two glucopyranosyl moieties

Table 1. ^{1}H NMR spectral data of compounds **3**–**6** and some derivatives (400 MHz, TMS)

3*	**7***	**4***	**4†**	**5***	**5†**	**8***	**6†**
1.37 *m*	1.72 *m*	1.45 *m*		2.28 *m*[a]		2.42 *m*[a]	1.19 *m*
1.66 *m*[a]	1.79 *m*	1.72 *m*		2.28 *m*[a]		2.42 *m*[a]	1.44 *m*[a]
1.84 *m*[b]	2.04 *m*	2.13 *m*		4.82 *ddd* (3.9, 7.8, 8.0)	4.38 *m*	4.88 *ddd* (3.9, 7.4, 8.0)	4.88 *m*
2.11 *m*	2.21 *m*	2.22 *m*					
6.82 *t* (3.7)	6.90 *t* (3.8)	6.89 *t* (3.9)	6.96 *t* (3.8)	6.82 *d* (3.9)	6.28 *d* (3.9)	6.80 *d* (3.9)	6.71 *d* (3.9)
5.54 *br d* (6.1)	5.65 *br d* (5.8)	5.56 *br d* (6.1)	5.54 *br d* (6.1)	5.18 *br d* (2.9)		5.08 *br d* (2.4)	5.19 *br d* (6.1)
1.84 *m*[b]	2.00 *m*	2.08 *br d* (12.2)		1.94 *m*	1.84 *m*[a]	2.07 *m*	1.78 *br d* (12.4)
2.25 *dd* (9.9, 14.8)	2.09 *m*	2.44 *ddd* (6.1, 6.1, 12.2)		2.90 *m*		2.49 *m*	2.16 *m*
3.18 *br d* (5.6)	2.81 *br d* (5.4)	3.36 *br d* (6.1)		3.68 *dd* (1.5, 12.0)		3.89 *dd* (2.7, 12.0)	2.88 *br d* (5.6)
1.66 *m*[a]	1.50 *dd* (1.7, 5.8)	1.90 *m*		2.33 *m*		2.46 *m*	1.44 *m*[a]
2.00 *dd* (5.0, 12.9)	1.97 *dd* (2.6, 14.5)	2.28 *m*[a]		1.77 *dd* (6.1, 14.0)	1.84 *m*[a]	2.03 *m*	1.70 *m*
2.05 *m*	2.29 *dd* (8.8, 14.5)	2.28 *m*[a]		1.92 *dd* (11.2, 14.0)	1.99 *dd* (5.8, 14.2)	2.11 *dd* (6.1, 14.0)	2.06 *br dd* (8.5, 15.0)
5.77 *br d* (9.3)	5.50 *br d* (8.8)	5.75 *br d* (8.3)	5.09 *br d* (8.5)	5.38 *dd* (6.1, 11.2)	5.45 *dd* (5.8, 11.2)	5.60 *dd* (6.1, 11.4)	5.16 *br d* (8.5)
6.91 *m*	6.94 *dd* (0.7, 1.7)	6.88 *dd* (0.7, 1.7)	6.50 *dd* (0.7, 1.7)	6.61 *dd* (1.0, 1.7)	6.49 *dd* (0.7, 1.8)	6.68 *dd* (0.7, 1.7)	6.67 *dd* (0.7, 1.7)
7.56 *dd* (1.5, 1.5)	7.60 *dd* (1.7, 1.7)	7.51 *dd* (1.7, 1.7)	7.57 *dd* (1.7, 1.7)	7.64 *dd* (1.0, 1.7)	7.55 *m*	7.66 *dd* (1.7, 1.7)	7.57 *dd* (1.7, 1.7)
8.13 *m*	7.85 *dd* (0.7, 1.7)	8.27 *m*	7.67 *dd* (0.7, 1.7)	7.74 *dd* (1.0, 1.7)	7.63 *m*	7.81 *dd* (0.7, 1.7)	7.65 *m*
1.31 *s*[c]	1.37 *s*	1.36 *s*	1.21 *s*	2.05 *s*	1.38 *s*	1.92 *s*	1.23 *s*
1.31 *s*[c]	1.44 *s*	1.43 *s*	1.18 *s*	1.10 *s*	0.78 *s*	1.87 *s*	1.14 *s*
3.63 *s*	3.67 *s*	3.64 *s*	3.66 *s*	3.61 *s*	3.64 *s*	3.63 *s*	3.69 *s*
4.87 *d* (7.6)		4.93 *d* (7.8)	4.19 *d* (7.8)	5.08 *d* (7.6)	4.46 *d* (7.8)		4.06 *d* (7.6)
		4.83 *d* (7.8)	4.06 *d* (7.8)				

·idine-d_5.
ISO-d_6.
·rlapped signals within a column.

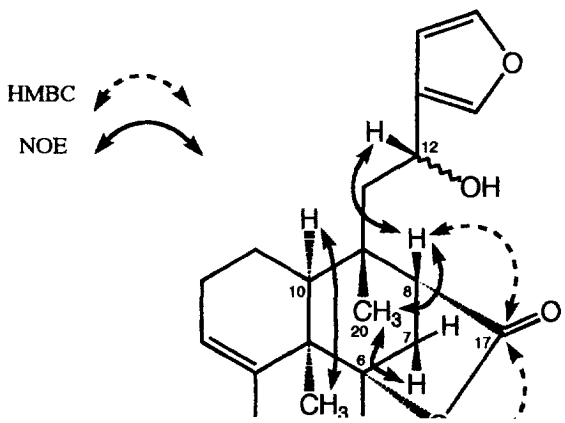
Table 2. ^{13}C NMR spectral data of compounds **3–6** and some derivatives (100 MHz, TMS)

C	**3***	**7***	**4***	**4†**	**5***	**5†**	**8***	**6†**
1	16.5 *t*	16.6 *t*	16.6 *t*	16.0 *t*	29.3 *t*	26.5 *t*	29.6 *t*	28.7 *t*
2	24.2 *t*	24.3 *t*	24.3 *t*	23.8 *t*	63.5 *d*	62.3 *d*	63.7 *d*	62.9 *d*
3	142.6 *d*	142.8 *d*	142.5 *d*	142.6 *d*	141.7 *d*	140.5 *d*	140.8 *d*	143.3 *d*
4	134.4 *s*	134.4 *s*	134.7 *s*	133.5 *s*	138.6 *s*	137.5 *s*	139.5 *s*	134.4 *s*
5	[a]39.4 *s*	[a]39.6 *s*	[a]39.6 *s*	38.6 *s*	42.3 *s*	41.0 *s*	41.7 *s*	38.5 *s*
6	82.8 *d*	82.8 *d*	82.8 *d*	82.0 *d*	79.1 *d*	76.8 *d*	67.9 *d*	81.9 *d*
7	29.5 *t*	29.6 *t*	29.6 *t*	28.5 *t*	27.8 *t*	28.2 *t*	28.9 *t*	27.6 *t*
8	46.8 *d*	47.6 *d*	47.1 *d*	46.0 *d*	41.7 *d*	40.5 *d*	40.8 *d*	48.7 *d*
9	[a]39.7 *s*	[a]39.8 *s*	[a]39.9 *s*	38.8 *s*	37.5 *s*	36.6 *s*	37.7 *s*	38.9 *s*
10	45.8 *d*	45.6 *d*	45.8 *d*	44.9 *d*	50.6 *d*	49.3 *d*	50.3 *d*	45.5 *d*
11	47.6 *t*	48.7 *t*	47.5 *t*	64.0 *t*	45.3 *t*	44.1 *t*	45.6 *t*	46.4 *t*
12	69.3 *d*	63.6 *d*	69.2 *d*	67.8 *d*	70.2 *d*	70.1 *d*	70.4 *d*	68.0 *d*
13	128.4 *s*	133.5 *s*	128.4 *s*	127.1 *s*	125.6 *s*	124.6 *s*	125.7 *s*	127.2 *s*
14	110.3 *d*	110.1 *d*	110.4 *d*	109.5 *d*	109.6 *d*	109.3 *d*	109.6 *d*	109.5 *d*
15	143.6 *d*	143.4 *d*	143.4 *d*	143.2 *d*	144.2 *d*	143.9 *d*	144.2 *d*	143.6 *d*
16	140.7 *d*	139.8 *d*	140.9 *d*	140.1 *d*	140.4 *d*	140.4 *d*	140.5 *d*	139.8 *d*
17	178.3 *s*	178.0 *s*	178.3 *s*	177.4 *s*	175.2 *s*	174.8 *s*	175.7 *s*	177.5 *s*
18	166.8 *s*	166.9 *s*	166.9 *s*	166.4 *s*	168.3 *s*	167.6 *s*	168.8 *s*	166.6 *s*
19	27.1 *q*	27.2 *q*	27.3 *q*	26.9 *q*	29.3 *q*	28.5 *q*	29.8 *q*	26.8 *q*
20	21.5 *q*	21.7 *q*	21.4 *q*	20.5 *q*	23.6 *q*	22.9 *q*	23.6 *q*	22.1 *q*
CH_3COO–	51.5 *q*	51.6 *q*	51.5 *q*	51.7 *q*	51.7 *q*	51.8 *q*	51.6 *q*	52.0 *q*
Glc 1′	101.4 *d*		101.2 *d*	99.6 *d*	106.6 *d*	104.8 *d*		99.9 *d*
2′	75.4 *d*		75.2 *d*	73.6 *d*	75.8 *d*	74.0 *d*		73.8 *d*
3′	78.5 *d*		78.3 *d*	76.7 *d*	78.6 *d*	77.5 *d*		76.8 *d*
4′	72.1 *d*		71.7 *d*	70.1 *d*	71.7 *d*	69.5 *d*		70.5 *d*
5′	78.1 *d*		76.9 *d*	75.7 *d*	78.0 *d*	76.7 *d*		76.8 *d*
6′	63.0 *t*		70.9 *d*	69.1 *d*	62.6 *t*	61.1 *t*		61.5 *t*
1″			105.4 *d*	103.5 *d*				
2″			75.4 *d*	73.6 *d*				
3″			78.4 *d*	76.9 *d*				
4″			72.2 *d*	70.7 *d*				
5″			78.4 *d*	76.8 *d*				
6″			62.8 *t*	61.2 *t*				

*In pyridine-d_5.
†In DMSO-d_6.
[a]Assignments may be interchanged in each column.

unit had to be joined with the other one at the C-6′-hydroxyl group as shown by the downfield shift of the ^{13}C NMR signal of C-6′ to δ 70.9 [3, 6–7]. Enzymatic hydrolysis of **4** with β-glucosidase yielded a partially hydrolysed compound, **3**. Further hydrolysis with crude hesperidinase yielded **7**. Hence, the structure of **4** was elucidated as shown.

Compounds **3** and **4** have physical and spectral data



identical to those of the known compounds borapetosides E and D, respectively [3]. However, while borapetosides E and D have their γ-lactone rings attached between C-4 and C-6, **3** and **4** have their γ-lactone rings attached between C-6 and C-8, as established by HMBC experiments which showed significant correlations between the H-6 and C-17 signals and between the H-8 and C-17 signals. Thus, it is suggested that the structures of borapetosides E and D should be revised/reanalysed.

Compound **5** has the molecular formula $C_{27}H_{36}O_{12}$, as determined by FAB-mass spectroscopy. In addition to the common structural features of **3–6**, the ^1H and ^{13}C, DEPT, ^1H–^1H COSY, PCHSH and HMBC spectra of **5** showed a signal corresponding to an oxygenated methine carbon (C-2). Also, the existence of a singlet signal at δ 175.2, attributable to an ester carbonyl (C-17), was observed. The position of the C-17 ester carbonyl was established on the basis of HMBC correlations between H-8 and C-17. As C-12 is an oxygen-bearing carbon it was deduced that the ester carbonyl is in a δ-lactone ring located between C-8 and C-12.

Enzymatic hydrolysis of **5** with crude hespiridinase gave D-glucose and an aglycone, **8**, with the molecular formula $C_{21}H_{26}O_7$. The attachment of the glucose moiety in **5** was determined to be at C-6, based on the glycosylation shift of the signal attributable to this carbon, δ 79.1 in **5** and δ 67.9 in **8** [6–7].

The relative configuration of **5** was established through **8** by NOE differential spectral measurements. The results showed that when the signal corresponding to H-10 was irradiated, NOEs were observed for the signals corresponding to H-12 and the Me-19 protons, while irradiation of the H-12 signal showed NOEs for the signals of H-10 and H-8. Irradiation of the signal of Me-19 protons gave rise to NOEs for the signals of H-10 and H-6. On irradiation of the H-6 signal, NOEs were observed for the signals of the Me-19 protons and H-8, while irradiation of the H-8 signal gave rise to NOEs for the signals of H-6 and H-12. Furthermore, irradiation of the signals corresponding to Me-20 protons gave rise to a NOE for the signal corresponding to H-2, while irradiation of the H-2 signal showed a NOE for the signal of the Me-20 protons. These results showed that H-10, Me-19, H-6, H-12, H-8 and the hydroxyl group attached to C-2 are located on the same side while Me-20 and the hydroxyl group at C-6 are located on the other side (Fig. 2). From these data the structure of **5** was identified as shown.

The physical and spectral data of **5** are very similar with those of the known compound borapetoside B (some values were differently assigned) [8]. However, the bond attaching the glucose moiety to C-6 in borapetoside B was assigned an α-configuration based on a comparison of the ^{13}C NMR data of borapetoside B with the reported data of closely related compounds.

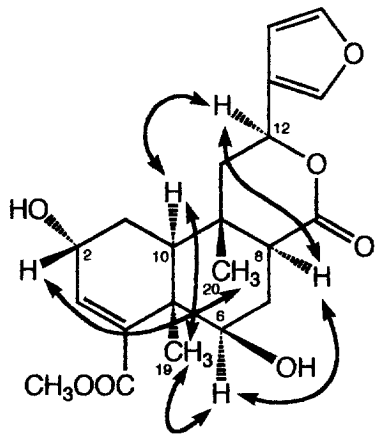


Fig. 2. Important NOES observed for **8**.

side, hand-in-hand with a close analysis of the structural model.

Compound **6** has the molecular formula $C_{27}H_{36}O_{12}$ on the basis of its high-resolution FAB-mass spectrum. In its ^{13}C NMR spectrum, a doublet signal at δ 62.9 corresponding to an oxygenated methine carbon was observed. Moreover, a singlet signal at δ 177.5 which is attributable to an ester carbonyl was also observed. Comparison of its spectral data with those of **3–5** showed that it has the same structure as **3** with an additional hydroxyl substituent at C-2 like **5**. The stereochemistry of **6** at various centres were deduced as shown. Compound **6** is a new compound and was given the name rumphioside I.

EXPERIMENTAL

General. Mp: uncorr; NMR: TMS as int. standard; HPLC: D-ODS-5 column (20.0 mm i.d. × 25 cm) with differential refractometer as detector; CC: Kieselgel 60 (70–230 mesh, Merck) and LiChroprep RP-18 (Merck); TLC: Silica gel 60 precoated plates, F_{254} (Merck); HPTLC: RP-18 precoated plates, F_{254} (Merck).

Plant material. Tinospora rumphii Boerl. was collected in Los Baños, Laguna, Philippines and authentication was done by Prof. Juan V. Pancho of the Department of Botany, Institute of Biological Sciences, University of the Philippines at Los Baños (UPLB). Voucher specimens are deposited at the Organic Chemistry and Natural Products Research Laboratory, Institute of Chemistry, UPLB and at the Department of Medicinal Chemistry of Natural Products, Institute of Pharmaceutical Sciences, Hiroshima University School of Medicine, Hiroshima, Japan.

Extraction and isolation of the diterpene glucosides. Air-dried powdered stems of *T. rumphii* (1.5 kg) were extracted with MeOH at room temp. After evapn of the solvent, the MeOH extract (125 g) was dissolved in H_2O and the soln was successively partitioned

11 frs (frs 1–11). Fr. 2 was further chromatographed over silica gel using stepwise elution with EtOAc–EtOH-H_2O (25:2:1, 20:2:1 and 8:2:1) to give Frs 2-1 to 2-7. Fr. 2-4 yielded **3** (40 mg) after HPLC; Fr. 2-5 yielded **2** (100 mg) and **1** (703 mg); Similarly, Fr. 4 was sepd into six frs, Frs 4-1 to 4-6, by silica gel CC using the same solvent system used for Fr. 2. Frs 4-1 and 4-2 gave **6** (11 mg) and **5** (1.8 g), respectively. Fr. 6 yielded **4** (186 mg) after subjecting it to silica gel CC followed by HPLC.

Borapetoside C (**1**). Needles from MeOH–H_2O, mp 121–122°. $[\alpha]_D^{22}$ −15.8° (MeOH; *c* 2.09).

Borapetoside F (**2**). Powder, $[\alpha]_D^{24}$ +81.1° (MeOH; *c* 1.06).

Compound **3**. Powder, $[\alpha]_D^{27}$ −75.8° (MeOH; *c* 1.49). FABMS (negative) *m/z*: 535.2183 $[C_{27}H_{36}O_{11} - H]^-$, requires 535.2179; ^{1}H NMR: Table 1; ^{13}C NMR: Table 2.

Enzymatic hydrolysis of **3**. Compound **3** (25 mg) was suspended in 8 ml H_2O and 25 mg of crude hespiridinase was added. The mixt. was incubated at 37° for 30 hr then extracted with EtOAc. The EtOAc extract was evapd *in vacuo* and the residue was purified by HPLC using 60% MeOH to give 4.5 mg of the aglycone **7**.

Compound **7**. Oil, $[\alpha]_D^{24}$ −34.8° (MeOH; *c* 0.29). FABMS (negative) *m/z*: 373.1641 $[C_{21}H_{26}O_6 - H]^-$, requires 373.1651; ^{1}H NMR: Table 1; ^{13}C NMR: Table 2.

Compound **4**. Powder, $[\alpha]_D^{26}$ −55.8° (MeOH; *c* 0.54). FABMS (negative) *m/z*: 697.2777 $[C_{33}H_{46}O_{16} - H]^-$, requires 697.2708. ^{1}H NMR: Table 1; ^{13}C NMR: Table 2.

Enzymatic hydrolysis of **4**. Compound **4** (150 mg) was dissolved in 12 ml H_2O and 50 mg of β-glucosidase was added. After incubation at 37° for 24 hr, the mixt. was diluted with an equiv. vol. of H_2O and then extracted with Et_2O. The Et_2O extract was evapd under red. pres. to give 60 mg of **3**. The sugar was identified as glucose by TLC comparison with an authentic sample. Compound **3** was further hydrolysed as described above to given **7**.

Compound **5**. Needles from MeOH–H_2O, mp 154–155°. $[\alpha]_D^{22}$ −8.6° (MeOH; *c* 1.28). FABMS (negative) *m/z*: 551.2146 $[C_{27}H_{36}O_{12} - H]^-$, requires 551.2128; ^{1}H NMR: Table 1; ^{13}C NMR: Table 2.

Enzymatic hydrolysis of **5**. Compound **5** (150 mg) was hydrolysed with crude hespiridinase (150 mg) for 48 hr using the same procedure used for **3**. After the usual work-up, the aglycone **8** was obtained.

Compound **8**. Amorphous solid, $[\alpha]_D^{22}$ −19.7° (MeOH; *c* 1.169); FABMS (negative) *m/z*: 389.1611 $[C_{21}H_{26}O_7 - H]^-$, requires 389.1600; ^{1}H NMR: Table 1; ^{13}C NMR: Table 2.

Rumphioside I (**6**). Powder, $[\alpha]_D^{24}$ −10.8° (MeOH; *c* 0.65). FABMS (negative) *m/z*: 551.2105 $[C_{27}H_{36}O_{12} - H]^-$, requires 551.2128; ^{1}H NMR: Table 1; ^{13}C NMR: Table 2.

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