Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Phytochemistry 65 (2004) 2003–2011
PHYTOCHEMISTRY
www.elsevier.com/locate/phytochem

Constituents from the bark of *Tabebuia impetiginosa*

Tsutomu Warashina *, Yoshimi Nagatani, Tadataka Noro

Institute for Environmental Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422-8526, Japan

Received 23 January 2004; received in revised form 20 April 2004
Available online 7 July 2004

Abstract

The bark of *Tabebuia impetiginosa* afforded nineteen glycosides, consisting of four iridoid glycosides, two lignan glycosides, two isocoumarin glycosides, three phenylethanoid glycosides and eight phenolic glycosides. Their structures were determined using both spectroscopic and chemical methods. Iridoid glycosides, phenylethanoid glycosides and lignan glycosides had ajugol, osmanthuside H and secoisolariciresinol 4-*O*-β-D-glucopyranoside as their structural elements, respectively, whereas the aglycone moieties of the isocoumarin glycosides were considered to be (−)-6-hydroxymellein. Phenolic glycosides had 4-methoxyphenol, 2,4-dimethoxyphenol, 3,4-dimethoxyphenol, 3,4,5-trimethoxyphenol and vanillyl 4-hydroxybenzoate as each aglycone moiety. Additionally, the sugar chains of these isocoumarin glycosides and phenolic glycosides were concluded to be β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside as well as those of osmanthuside H and above phenylethanoid glycosides.

Keywords: Tabebuia impetiginosa; Bignoniaceae; Iridoid; Lignan; Isocoumarin; Phenylethanoid; Phenolic glycoside

1. Introduction

Tabebuia impetiginosa is distributed throughout southeast Latin America and is a national flower of Brazil (Hashimoto, 1996), and has been used in folk medicine as a diuretic and an astringent (Hashimoto, 1996). In the course of our research on phytochemicals from Brazilian plants, we have started to study the constituents present in hydrotropic fraction of the MeOH extract from the bark of *T. impetiginosa*. The present paper describes the isolation and structural determination of 16 new glycosides along with three known ones (**1** (Nakano et al., 1993), **2** (Nakano et al., 1993) and **4** (Opitz et al., 1999)).

2. Results and discussion

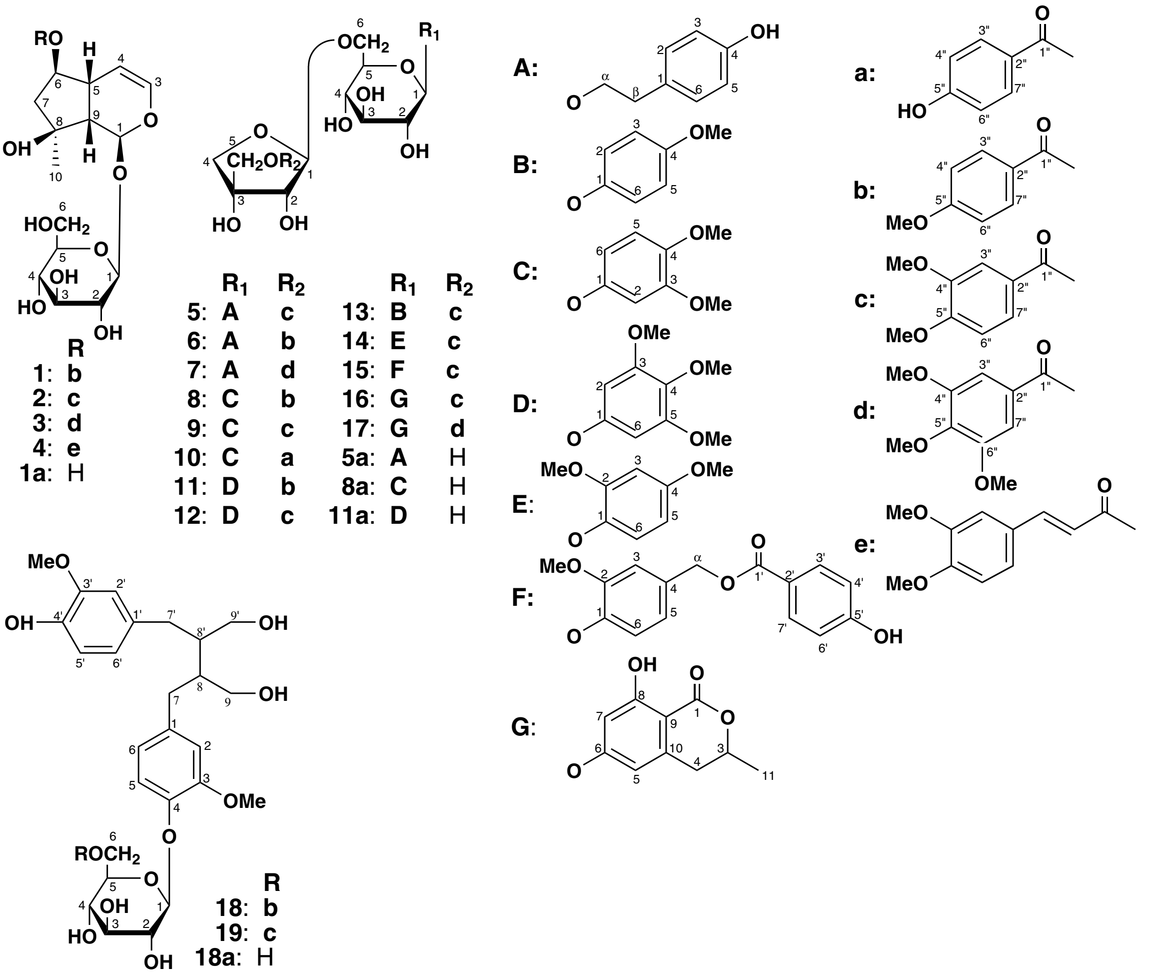
The MeOH extract from the bark of *T. impetiginosa* was suspended in water. The suspension was extracted with diethyl ether and partitioned into an ether-soluble fraction and a water-soluble fraction. The water-soluble fraction was passed through a porous polymer gel "Mitsubishi Diaion HP-20″ column and the adsorbed material was subsequently eluted with MeOH–H_2O (1:1), then MeOH–H_2O (7:3) and finally MeOH. The MeOH–H_2O (7:3) eluate from the Diaion HP-20 column was concentrated and the residue subjected to a silica gel column and semi-preparative HPLC thereby affording compounds (**1**–**19**). The structural determination of known compounds **1**, **2** and **4** was made based on comparison of the NMR spectral data with the literature data (Nakano et al., 1993; Opitz et al., 1999).

Compound **3** was suggested to have the molecular formula $C_{25}H_{34}O_{13}$ based on high resolution (HR)-FABMS [m/z 565.1871 $[M+Na]^+$]. On comparing the ^1H and ^{13}C NMR spectra of **3** with those of known compounds **1** and **2**, signals derived from ajugol (**1a**) (Nakano et al., 1993) were also observed. But the proton signals of the ester moiety resonates at δ 7.36 (2H, *s*) and δ 3.89 (6H, *s*) and δ 3.83 (3H, *s*), instead of those of the 4-methoxybenzoyl and 3,4-dimethoxybenzoyl groups in **1** and **2**. Furthermore, release of 3,4,5-trimethoxybenzoic acid with ajugol by alkaline hydrolysis of **3** sug-

---

* Corresponding author. Tel./fax: +81-54-264-5791.
E-mail address: warashin@sea.u-shizuoka-ken.ac.jp (T. Warashina).

0031-9422/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.phytochem.2004.06.012



	R
1:	b
2:	c
3:	d
4:	e
1a:	H

	R_1	R_2
5:	A	c
6:	A	b
7:	A	d
8:	C	b
9:	C	c
10:	C	a
11:	D	b
12:	D	c
13:	B	c
14:	E	c
15:	F	c
16:	G	c
17:	G	d
5a:	A	H
8a:	C	H
11a:	D	H

	R
18:	b
19:	c
18a:	H

gested that compound **3** consisted of ajugol and the 3,4,5-trimethoxybenzoyl group. Additionally, because the H-6 signal was observed at δ 5.06 (1H, *m*) as well as **1** and **2**, this 3,4,5-trimethoxybenzoyl group was deduced to be located at the C-6-OH position of ajugol. Accordingly, the structure of **3** was determined to be 6-*O*-(3,4,5-trimethoxybenzoyl)-ajugol.

The molecular formulae of compounds **5**, **6** and **7** were considered to be $C_{28}H_{36}O_{14}$, $C_{27}H_{34}O_{13}$ and $C_{29}H_{38}O_{15}$ on the basis of HR-FABMS, respectively. The ^{1}H NMR spectra of these three compounds commonly showed the presence of methylene protons, a glucosyl anomeric proton, an apiosyl anomeric proton and aromatic protons. The products from **5**–**7** by alkaline hydrolysis were determined to be osmanthuside H (**5a**) (Sugiyama and Kikuchi, 1993) by the ^{1}H and ^{13}C NMR spectral measurements and/or HPLC analysis. At the same time, alkaline hydrolysis yielded 3,4-dimethoxybenzoic acid from **5**, 4-methoxybenzoic acid from **6** and 3,4,5-trimethoxybenzoic acid from **7**. In the heteronuclear multiple-bond connectivity (HMBC) experiment in **5**, observation of long-range correlations between the carbonyl carbon signal of the 3,4-dimethoxybenzoyl group (δ 167.6) and H-5 signals of β-D-apiofuranose [δ 4.37 (1H, *d*, $J = 11.5$ Hz) and 4.36 (1H, *d*, $J = 11.5$ Hz)] indicated that the 3,4-dimethoxybenzoyl group was attached to C-5-OH of β-D-apiofuranose. Thus, structure **5** was elucidated to be 2-(4-hydroxyphenyl)ethyl 1-*O*-β-D-[5-*O*-(3,4-dimethoxybenzoyl)]-apiofuranosyl-(1 → 6)-β-D-glucopyranoside. Because of the similarities of the ^{1}H and ^{13}C NMR spectral data of **6** and **7** with those of **5**, osmanthusides *I* and *J* (Sugiyama and Kikuchi, 1993) (except for the signals due to the ester moieties), the structures of **6** and **7** were established as shown.

Compounds **8**, **9** and **10** had the molecular formulae, $C_{27}H_{34}O_{14}$, $C_{28}H_{36}O_{15}$, and $C_{26}H_{32}O_{14}$, respectively, on the basis of HR-FABMS analyses. Alkaline hydrolysis of **8** produced **8a** whose molecular formula was deduced as $C_{19}H_{28}O_{12}$ from its HR-FABMS, as well as 4-methoxybenzoic acid. Comparison of the ^{1}H and ^{13}C NMR spectral data of **8a** with those of osmanthuside H (**5a**) (Sugiyama and Kikuchi, 1993) suggested that the sugar moiety of **8a** was also β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside. The ^{1}H NMR spectrum of **8a** that the ABX-type aromatic proton signals [δ 6.87 (1H, *d*,

$J = 8.5$ Hz), 6.78 (1H, *d*, $J = 2.5$ Hz), 6.69 (1H, *dd*, $J = 8.5, 2.5$ Hz)] and two methoxyl proton signals [δ 3.82 (3H, *s*), 3.78 (3H, *s*)] as the signals due to the aglycone moiety. In the difference nuclear Overhauser effect (NOE) experiments in **8a**, NOEs were observed as follows; δ 4.74 (H-1 of β-D-glucopyranose) and δ 6.78, 6.69; δ 3.78 (—OMe) and δ 6.87; δ 3.82 (—OMe) and δ 6.78. These results indicates that the aglycone moiety of **8a** was 3,4-dimethoxyphenol, this being confirmed by acid hydrolysis following alkaline hydrolysis (Section 3). Accordingly, compound **8a** was 3,4-dimethoxyphenyl 1-*O*-β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside. In compound **8**, the attached position of the acyl group was considered to be C-5-OH of β-D-apiofuranose, according to comparison of the ^{1}H and ^{13}C NMR spectral data of the apiofuranosyl moiety in **8** with those in **5**–**7**. On the basis of the above evidence, structure **8** was established to be 3,4-dimethoxyphenyl 1-*O*-β-D-[5-*O*-(4-methoxybenzoyl)]-apiofuranosyl-(1 → 6)-β-D-glucopyranoside. Alkaline hydrolysis of **9** and **10**, respectively, produced 3,4-dimethoxybenzoic acid and 4-hydroxybenzoic acid together with **8a**. Thus, by comparison with the ^{1}H and ^{13}C NMR spectral data to the apiofuranosyl moieties in **8**–**10**, the structures of **9** and **10** were determined as shown.

Compounds **11** and **12** had the molecular formulae, $C_{28}H_{36}O_{15}$ and $C_{29}H_{38}O_{16}$, respectively, as deduced from HR-FABMS analyses. The ^{1}H and ^{13}C NMR spectra of **11** and **12** revealed the presence of one 1,3,4,5-tetrasubstituted symmetrical aromatic ring, one methoxyl and two equivalent methoxyl groups with the β-D-(5-*O*-acyl)-apiofuranosyl-(1 → 6)-β-D-glucopyranosyl unit. Alkaline hydrolysis of **11** afforded 3,4,5-trimethoxyphenol 1-*O*-β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside (**11a**) (Kanchanapoom et al., 2002) together with 4-methoxybenzoic acid. Similarly, alkaline hydrolysis of **12** yielded **11a** and 3,4-dimethoxybenzoic acid. Thus, the structures of **11** and **12** were determined as shown.

The molecular formulae of compounds **13**, **14** and **15** were $C_{27}H_{34}O_{14}$, $C_{28}H_{36}O_{15}$ and $C_{35}H_{40}O_{17}$ on HR-FABMS. The analyses of the ^{1}H and ^{13}C NMR spectra suggested that they had the β-D-[5-*O*-(3,4-dimethoxybenzoyl)]-apiofuranosyl-(1 → 6)-β-D-glucopyranosyl unit as the sugar and ester moieties. Because acid hydrolysis following alkaline hydrolysis showed the aglycone of **13** was 4-methoxyphenol, the structure of **13** was concluded to be 4-methoxyphenyl 1-*O*-β-D-[5-*O*-(3,4-dimethoxybenzoyl)]-apiofuranosyl-(1 → 6)-β-D-glucopyranoside. Compound **14**, the AMX-type aromatic proton signals [δ 7.04 (1H, *d*, $J = 9.0$ Hz), 6.52 (1H, *d*, $J = 2.5$ Hz), 6.33 (1H, *dd*, $J = 9.0, 2.5$ Hz)] and two methoxyl signals [δ 3.80 (3H, *s*), 3.68 (3H, *s*)] observed in the ^{1}H NMR spectrum indicated that the aglycone of **14** was a trisubstituted-phenyl group. In the difference NOE spectra, **14** had showed the NOEs between δ 4.67 (H-1 of β-D-glucopyranose) and δ 7.04; δ 3.80 (—OMe) and δ 6.52; 3.68 (—OMe) and δ 6.52, 6.33. These results suggested that the aglycone of **14** was 2,4-dimethoxyphenol, and **14** was determined to be 2,4-dimethoxyphenol 1-*O*-β-D-[5-*O*-3,4-dimethoxybenzoyl)]-apiofuranosyl-(1 → 6)-β-D-glucopyranoside. Alkaline hydrolysis of **15** yielded 4-hydroxybenzoic acid with 3,4-dimethoxybenzoic acid being located at the C-5-OH position of β-D-apiofuranose, and acid hydrolysis following alkaline hydrolysis afforded vanillyl alcohol together with D-glucose and apiose. In the HMBC spectrum, long-range correlations were observed between the carbonyl carbon signal of this 4-hydroxybenzoyl group (δ 168.0) and the hydroxy methylene proton signals of vanillyl alcohol [δ 5.13 (2H, *s*)]. Thus, the aglycone moiety was deduced to be vanillyl 4-hydroxybenzoate. The attached position of β-D-[5-*O*-(3,4-dimethoxybenzoyl)]-apiofuranosyl-(1 → 6)-β-D-glucopyranosyl unit was confirmed by irradiation of the anomeric proton signal of β-D-glucopyranose in the difference NOE experiment. Namely, an NOE was observed for this anomeric proton signal [δ 4.83 (1H, *d*, $J = 8.0$ Hz)] and the H-6 signal of vanillyl alcohol [δ 7.12 (1H, *d*, $J = 8.0$ Hz)]. On above findings, structure of **15** was established as shown.

Compounds **16** and **17** were deduced to have the molecular formulae, $C_{30}H_{36}O_{16}$ and $C_{31}H_{38}O_{17}$ following the analysis of the HR-FABMS. The ^{1}H and ^{13}C NMR spectra revealed signals due to β-D-[5-*O*-(3,4-dimethoxybenzoyl)]-apiofuranosyl-(1 → 6)-β-D-glucopyranosyl unit in **16** and β-D-[5-*O*-(3,4,5-trimethoxybenzoyl)]-apiofuranosyl-(1 → 6)-β-D-glucopyranosyl unit in **17**, together with the same signals due to the aglycone moieties in both compounds. Acid hydrolysis of **16** afforded the aglycone (**16a**) which was identified to be (−)-6-hydroxymellein on the basis of comparison of the ^{1}H NMR, CD spectral data and optical rotation value (Breinholt et al., 1993; Antus et al., 1983; Venkatasubbaiah and Chilton, 1991). In the difference NOE spectrum in **16**, irradiation of the anomeric proton signal of β-D-glucopyranose [δ 4.93 (1H, *d*, $J = 8.0$ Hz)] revealed NOEs corresponding the signals of H-5 [δ 6.39 (1H, *d*, $J = 2.5$ Hz)] and H-7 [δ 6.51 (1H, *d*, $J = 2.5$ Hz)] of the aglycone. Thus, the above esterified sugar moiety attached to the C-6 position of (−)-6-hydroxymellein, and the structures of **16** and **17** were determined to be as shown.

The molecular formulae of compounds **18** and **19** were $C_{34}H_{42}O_{13}$ and $C_{35}H_{44}O_{14}$ by HR-FABMS, with their ^{1}H and ^{13}C NMR spectra of **18** and **19** being similar to that of glehlinoside A (Yuan et al., 2002). Additionally, the ester moieties of **18** and **19** were concluded to be 4-methoxybenzoic acid and 3,4-dimethoxybenzoic acid, respectively, according to the interpretation of the ^{1}H, ^{13}C NMR spectral measurements and the results for alkaline hydrolysis; alkaline hydrolysis of **18** produced compound **18a**, which was determined to be secoisolariciresinol 4-*O*-β-D-glucopyranoside by interpretations of the ^{1}H and ^{13}C NMR spectral data (Yuan et al., 2002) although optical rotation data for **18a** differs from the literature value (Yuan et al., 2002). Thus, it was not possible to assign absolute configuration of the aglycone moiety of **18** as either 8*R*, $8'^{R}$-secoisolariciresinol or 8*S*, 8′*S*-secoisolariciresinol. Acid hydrolysis of **18a** and **18** could not be carried out due to insufficient materials. Thus, the deduced structures of **18** and **19** are as shown.

3. Experimental

Optical rotation and circular dichroism measurements were obtained using a JASCO-DIP1000 digital polarimeter and a JASCO J-20A automatic recording spectropolarimeter, respectively. FABMS spectra were collected on a JEOL JMS-700 spectrometer in *m*-nitrobenzyl alcohol, whereas both ^{1}H and ^{13}C NMR spectra were recorded in MeOH-d_4 solution on a JEOL JNM A-400 (400 and 100.40 MHz, respectively), spectrometer. Chemical shifts are given in the δ (ppm) with tetramethylsilane (TMS) as an internal standard, UV spectra measured a Beckman UV640 spectrometer, whereas CG utilized a Hitachi G-3000 gas chromatograph and HPLC analyses employed a JASCO 800 system instrument.

3.1. Plant material

The bark of *Tabebuia impetiginosa* was purchased in San Paulo-city, Brazil, in 2000, and identified by Y. Nagatani.

3.2. Extraction and isolation

The bark of *Tabebuia impetiginosa* (935 g) was extracted three times with MeOH under reflux. The extract was then concentrated under reduced pressure with the resulting residue suspended in H_2O. Following its extraction with Et_2O, the H_2O layer was passed through a porous polymer gel “Mitsubishi Diaion HP-20” column with adsorbed material being eluted with MeOH–H_2O (1:1), MeOH–H_2O (7:3) and MeOH, respectively. The MeOH–H_2O (7:3) fraction from the Diaion HP-20 column was then evaporated to dryness, with the residue (23.0 g) subject to silica gel CC with a $CHCl_3$–MeOH–EtOAc–H_2O (50:10:38:1) eluant to get five fractions (A (1.9 g), B (1.6 g), C (6.0 g), D (4.0 g) and E (8.0 g). Using semi-preparative HPLC (Develosil-ODS-15/30, —C8 and YMC-ODS: 25–30% MeCN in water and 40–50% MeOH in water), the fraction B (1.6 g) afforded compounds **8** (40 mg), **11** (65 mg), **13** (4 mg), **14** (4 mg), **15** (9 mg), **16** (32 mg), **17** (4 mg), **18** (6 mg), **19** (4 mg). Similarly, the fractions C (2.1 g) and D (50 mg) afforded compounds **3** (45 mg), **4** (7 mg), **5** (44 mg), **6** (32 mg), **7** (5 mg), **9** (32 mg), **10** (7 mg), **12** (8 mg) and **1** (25 mg), **2** (14 mg), respectively.

Compound **3**: Amorphous powder. $[\alpha]_D^{22}$ – 130° (MeOH; *c* 2.65). UV λ_{max}^{MeOH} nm (log ε): 213 (4.53), 265 (4.03), 286 (sh). FABMS *m*/*z*: 565 $[M+Na]^+$, HR-FABMS *m*/*z*: 565.1871 (Calcd. for $C_{25}H_{34}O_{13}Na$: 565.1897). ^{13}C NMR (MeOH-d_4 at 35 °C): δ 167.4 (C-1″), 154.4 × 2 (C-4″, -6″), 143.8 (C-5″), 141.3 (C-3), 126.9 (C-2″), 108.3 × 2 (C-3″, -7″), 104.5 (C-4), 99.4 (C_{Glc}-1), 93.5 (C-1), 81.2 (C-6), 79.2 (C-8), 78.2, 78.0 (C_{Glc}-3, -5), 74.8 (C_{Glc}-2), 71.8 (C_{Glc}-4), 62.9 (C_{Glc}-6), 61.2 (C-5″–OMe), 56.8 × 2 (C-4″, -6″–OMe), 51.9 (C-9), 47.7 (C-7), 39.6 (C-5), 26.2 (C-10). ^{1}H NMR (MeOH-d_4 at 35 °C): δ 7.36 (2H, *s*, H-3″, -7″), 6.24 (1H, *dd*, $J = 6.5$, 2.5 Hz, H-3), 5.06 (1H, *m*, H-6), 5.51 (1H, *d*, $J = 2.5$ Hz, H-1), 5.00 (1H, *dd*, $J = 6.5$, 2.5 Hz, H-4), 4.68 (1H, *d*, $J = 8.0$ Hz, H_{Glc}-1), 3.90 (overlapping, H_{Glc}-6), 3.89 (6H, *s*, C-4″, -6″–OMe), 3.83 (3H, *s*, C-5″–OMe), 3.67 (1H, *dd*, $J = 12.0$, 5.5 Hz, H_{Glc}-6), 3.38 (1H, *t*, $J = 8.0$ Hz, H_{Glc}-3), 3.32 (1H, *m*, H_{Glc}-5), 3.27 (1H, *t*, $J = 8.0$ Hz, H_{Glc}-4), 3.20 (1H, *t*, $J = 8.0$ Hz, H_{Glc}-2), 3.02 (1H, *m*, H-5), 2.63 (1H, *dd*, $J = 9.5$, 2.5 Hz, H-9), 2.29 (1H, *dd*, $J = 14.5$, 6.0 Hz, H-7), 2.07 (1H, *dd*, $J = 14.5$, 3.5 Hz, H-7), 1.42 (3H, *s*, H-10).

Compound **5**: Amorphous powder. $[\alpha]_D^{22}$ –51.6° (MeOH; *c* 2.15). UV λ_{max}^{MeOH} nm (log ε): 201 (4.46), 219 (4.39), 261 (4.03), 286 (3.76). FABMS *m*/*z*: 619 $[M+Na]^+$, HR-FABMS *m*/*z*: 619.2007 (Calcd. for $C_{28}H_{36}O_{14}Na$: 619.2002). For ^{13}C and ^{1}H NMR spectra, see Tables 1 and 2. ^{1}H NMR spectrum of aglycone moiety: δ 7.00 (2H, *d*, $J = 8.0$ Hz, H-2, -6), 6.67 (2H, *d*, $J = 8.0$ Hz, H-3, -5), 3.94 (1H, *ddd*, $J = 9.5$, 8.0, 6.5 Hz, H-α), 3.67 (1H, *ddd*, $J = 9.5$, 8.0, 6.5 Hz, H-α), 2.77 (2H, *m*, H-β).

Compound **6**: Amorphous powder. $[\alpha]_D^{22}$ –55.4° (MeOH; *c* 1.93). UV λ_{max}^{MeOH} nm (log ε): 202 (4.88), 219 (sh), 256 (4.48). FABMS *m*/*z*: 589 $[M+Na]^+$, HR-FABMS *m*/*z*: 589.1893 (Calcd. for $C_{27}H_{34}O_{13}Na$: 589.1897). For ^{13}C and ^{1}H NMR spectra, see Tables 1 and 2. The ^{1}H NMR spectrum of the aglycone moiety was in good agreement with that of **5**.

Compound **7**: Amorphous powder. $[\alpha]_D^{22}$ – 54° (MeOH; *c* 0.51). UV λ_{max}^{MeOH} nm (log ε): 214 (4.56), 267 (4.05), 291 (sh). FABMS *m*/*z*: 649 $[M+Na]^+$, HR-FABMS *m*/*z*: 649.2114 (Calcd. for $C_{29}H_{38}O_{15}Na$: 649.2108). For ^{13}C and ^{1}H NMR spectra, see Tables 1 and 2. The ^{1}H NMR spectrum of the aglycone moiety was in good agreement with that of **5**.

Compound **8**: Amorphous powder. $[\alpha]_D^{22}$ –76.0° (MeOH; *c* 1.79). UV λ_{max}^{MeOH} nm (log ε): 202 (4.89), 230 (3.96), 256 (4.20). FABMS *m*/*z*: 605 $[M+Na]^+$, HR-FABMS *m*/*z*: 605.1836 (Calcd. for $C_{27}H_{34}O_{14}Na$: 605.1846). For ^{13}C and ^{1}H NMR spectra, see Tables 1 and 2. ^{1}H NMR spectrum of the aglycone moiety: δ 6.77 (1H, *d*, $J = 8.5$ Hz, H-5), 6.74 (1H, *d*, $J = 2.5$ Hz, H-2),

Table 1
^{13}C NMR spectral data for compounds **5**–**17**

No.	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
C-α	72.1	72.1	72.1	–	–	–	–	–	–	–	67.2	–	–
-β	36.4	36.4	36.4	–	–	–	–	–	–	–	–	–	–
-1	130.8	130.8	130.8	153.8	153.8	153.8	155.9	155.9	153.2	142.0	147.9	171.2	171.2
-2	130.9	130.9	130.9	104.5	104.5	104.5	96.7	96.7	119.3	152.1	150.9	–	–
-3	116.1	116.1	116.1	151.1	151.1	151.1	154.8	154.8	115.5	101.6	113.9	77.2[a]	77.2[a]
-4	156.7	156.7	156.8	146.2	146.2	146.2	134.8	134.9	156.6	157.6	132.6	35.4	35.4
-5	116.1	116.1	116.1	114.0	114.0	114.1	154.8	154.8	115.5	105.4	122.3	108.6	108.6
-6	130.9	130.9	130.9	109.4	109.3	109.4	96.7	96.7	119.3	120.1	118.1	165.1[b]	165.2[b]
-7	–	–	–	–	–	–	–	–	–	–	–	103.4	103.1
-8	–	–	–	–	–	–	–	–	–	–	–	164.9[b]	164.9[b]
-9	–	–	–	–	–	–	–	–	–	–	–	103.8	103.7
-10	–	–	–	–	–	–	–	–	–	–	–	143.1	143.0
-11	–	–	–	–	–	–	–	–	–	–	–	20.8	20.8
—OMe	–	–	–	56.5	56.5[a]	56.6	56.7 × 2	56.7 × 2	56.0	56.0	56.8	–	–
	–	–	–	57.1	57.1	57.2	61.2	61.2	–	56.7[a]	–	–	–
-1′	–	–	–	–	–	–	–	–	–	–	168.0	–	–
-2′	–	–	–	–	–	–	–	–	–	–	122.3	–	–
-3′	–	–	–	–	–	–	–	–	–	–	132.8	–	–
-4′	–	–	–	–	–	–	–	–	–	–	116.2	–	–
-5′	–	–	–	–	–	–	–	–	–	–	163.6	–	–
-6′	–	–	–	–	–	–	–	–	–	–	116.2	–	–
-7′	–	–	–	–	–	–	–	–	–	–	132.8	–	–
Sugar moieties													
Glc-1	104.4	104.4	104.4	103.5	103.5	103.4	103.3	103.3	103.5	104.1	102.8	101.3	101.2
-2	75.1[a]	75.1[a]	75.1[a]	75.0[a]	75.0[b]	75.1[a]	75.0[a]	75.0[a]	75.0[a]	75.0	75.1[a]	74.7[c]	74.7[c]
-3	78.1	78.1	78.1	78.0	78.0	78.0	77.9	78.0	78.1	77.9	77.9	77.9	77.9
-4	71.8	71.7	71.8	71.7	71.7	71.7	71.5	71.5	71.8	71.8	71.8	71.7	71.8
-5	76.8	76.8	76.9	76.9	76.9	76.9	76.9	76.9	76.9	77.0	77.0	77.1[a]	77.1[a]
-6	68.6	68.6	68.6	68.5	68.6	68.6	68.3	68.3	68.7	68.7	68.8	69.0	69.5
Api-1	110.7	110.7	110.8	110.7	110.7	110.7	110.5	110.5	110.8	110.8	110.9	111.0	111.4
-2	78.6	78.5	78.6	78.6	78.7	78.6	78.6	78.7	78.7	78.7	78.6	78.8[d]	78.9
-3	79.0	79.0	79.1	78.9	79.0	79.0	79.0	79.0	79.0	79.0	79.0	78.9[d]	78.9
-4	75.0[a]	75.0[a]	75.0[a]	74.9[a]	74.9[b]	75.0[a]	74.9[a]	74.9[a]	75.0[a]	75.0	74.9[a]	75.1[c]	75.1[c]
-5	67.8	67.6	68.3	67.6	67.7	67.5	67.6	67.8	67.7	67.6	67.6	67.6	67.7
Ester moieties													
C-1″	167.6	167.6	167.4	167.6	167.6	167.9	167.6	167.7	167.7	167.6	167.6	167.6	167.3
-2″	123.5	123.3	126.4	123.3	123.5	122.1	123.3	123.5	123.5	123.5	123.5	123.5	126.3
-3″	113.7	132.8	108.4	132.8	113.8	133.0	132.8	113.8	113.8	113.8	113.8	113.7	108.3
-4″	150.2	114.8	154.5	114.9	150.2	116.2	114.9	150.3	150.3	150.2	150.2	150.1	154.3
-5″	155.0	165.3	143.9	165.3	155.0	163.7	165.3	155.0	155.1	155.0	155.0	154.9	143.7
-6″	112.1	114.8	154.5	114.9	112.1	116.2	114.9	112.1	112.1	112.1	112.1	112.0	154.3
-7″	125.1	132.8	108.4	132.8	125.1	133.0	132.8	125.1	125.2	125.1	125.1	125.1	108.3
—OMe	56.5	56.0	56.9 × 2	56.0	56.5	–	56.0	56.5	56.5	56.5[a]	56.5	56.5 × 2	56.8 × 2
	56.6	–	61.2	–	56.6[a]	–	–	56.6	56.6	56.6[a]	56.6	–	61.2

Measured in MeOH-d_4 solution at 35 °C.

[a–d] Interchangeable in each column.

Table 2
^{1}H NMR spectral data of the sugar and ester moieties of compounds **5**–**19**

No.	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Sugar moieties							
Glc-1	4.26 (*d*, 8.0)	4.26 (*d*, 8.0)	4.25 (*d*, 8.0)	4.74[a]	4.72 (*d*, 8.0)	4.74[a]	4.79 (*d*, 8.0)
-2	3.19 (*t*, 8.0)	3.19 (*t*, 8.0)	3.18 (*t*, 8.0)	3.43[a]	3.42[a]	3.43[a]	3.44[a]
-3	3.34 (*t*, 8.0)	3.34 (*t*, 8.0)	3.34[a]	3.43[a]	3.42[a]	3.43[a]	3.44[a]
-4	3.28 (*t*, 8.0)	3.28 (*t*, 8.0)	3.26 (*t*, 8.5)	3.34 (*t*, 8.5)	3.33[a]	3.33[a]	3.35 (*t*, 8.5)
-5	3.40 (*m*)	3.40 (*m*)	3.40 (*m*)	3.54 (*m*)	3.54 (*m*)	3.54 (*m*)	3.56 (*m*)
-6	4.01 (*dd*, 11.5, 2.0)	4.01 (*dd*, 11.0, 2.0)	4.00 (*dd*, 10.5, 2.0)	4.05 (*dd*, 11.5, 2.0)	4.05 (*dd*, 11.0, 2.0)	4.05 (*dd*, 10.5, 2.0)	4.06 (*dd*, 11.5, 2.0)
	3.63 (*dd*, 11.5, 6.0)	3.63 (*dd*, 11.0, 6.0)	3.63 (*dd*, 10.5, 6.0)	3.63 (*dd*, 11.5, 6.5)	3.62 (*dd*, 11.0, 6.5)	3.62 (*dd*, 10.5, 6.5)	3.63 (*dd*, 11.5, 6.5)
Api-1	5.05 (*d*, 2.0)	5.05 (*d*, 2.0)	5.05 (*d*, 2.0)	5.02 (*d*, 2.0)	5.02 (*d*, 2.0)	5.02 (*d*, 2.0)	5.01 (*d*, 2.0)
-2	4.01 (*d*, 2.0)	4.00 (*d*, 2.0)	4.00 (*d*, 2.0)	3.99 (*d*, 2.0)	4.00 (*d*, 2.0)	3.98 (*d*, 2.0)	3.96 (*d*, 2.0)
-4	4.09 (*d*, 10.0)	4.09 (*d*, 10.0)	4.08 (*d*, 10.0)	4.08 (*d*, 10.0)	4.09 (*d*, 10.0)	4.07 (*d*, 10.0)	4.08 (*d*, 10.0)
	3.88 (*d*, 10.0)	3.87 (*d*, 10.0)	3.88 (*d*, 10.0)	3.86 (*d*, 10.0)	3.86 (*d*, 10.0)	3.86 (*d*, 10.0)	3.86 (*d*, 10.0)
-5	4.37 (*d*, 11.5)	4.37 (*d*, 11.5)	4.40 (*d*, 11.5)	4.38 (*d*, 12.0)	4.39 (*d*, 12.0)	4.45 (*d*, 11.5)	4.36 (*d*, 11.5)
	4.36 (*d*, 11.5)	4.34 (*d*, 11.5)	4.38 (*d*, 11.5)	4.34 (*d*, 12.0)	4.35 (*d*, 12.0)	4.43 (*d*, 11.5)	4.31 (*d*, 11.5)
Ester moieties							
-3″	7.56 (*d*, 2.0)	7.98 (*brd*, 8.5)	7.35 (*s*)	7.99 (*d*, 8.5)	7.56 (*d*, 2.0)	7.91 (*brd*, 8.5)	7.95 (*d*, 8.5)
-4″	–	6.97 (*brd*, 8.5)	–	6.97 (*d*, 8.5)	–	6.82 (*brd*, 8.5)	6.97 (*d*, 8.5)
-6″	6.99 (*d*, 8.0)	6.97 (*brd*, 8.5)	–	6.97 (*d*, 8.5)	6.99 (*d*, 8.0)	6.82 (*brd*, 8.5)	6.97 (*d*, 8.5)
-7″	7.69 (*dd*, 8.0, 2.0)	7.98 (*brd*, 8.5)	7.35 (*s*)	7.99 (*d*, 8.5)	7.69 (*dd*, 8.0, 2.0)	7.91 (*brd*, 8.5)	7.95 (*d*, 8.5)
—OMes	3.88 (*s*)	3.85 (*s*)	3.87 (*s*)x2	3.84 (*s*)	3.88 (*s*)		3.85 (*s*)
	3.85 (*s*)	–	3.82 (*s*)	–	3.84 (*s*)		–

No.	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
Sugar moieties								
Glc-1	4.77 (*d*, 8.0)	4.69 (*d*, 8.0)	4.67 (*d*, 8.5)	4.83 (*d*, 8.0)	4.93 (*d*, 8.0)	4.93 (*d*, 8.0)	4.85 (*d*, 8.0)	4.84 (*d*, 8.0)
-2	3.43[a]	3.41[a]	3.41 (*t*, 8.5)	3.50 (*t*, 8.0)	3.46[a]	3.45[a]	3.52[a]	3.52[a]
-3	3.43[a]	3.41[a]	3.44 (*t*, 8.5)	3.44 (*t*, 8.0)	3.46[a]	3.45[a]	3.52[a]	3.52[a]
-4	3.35 (*t*, 8.5)	3.32[a]	3.32[a]	3.32[a]	3.33[a]	3.27[a]	3.44 (*t*, 8.5)	3.44 (*t*, 8.5)
-5	3.55 (*m*)	3.52 (*m*)	3.48 (*m*)	3.56 (*m*)	3.67 (*m*)	3.71 (*m*)	3.75 (*m*)	3.75 (*m*)
-6	4.06 (*dd*, 11.0, 2.0)	4.04 (*dd*, 11.0, 2.0)	4.01 (*dd*, 11.0, 2.0)	4.04 (*dd*, 11.0, 2.0)	4.05 (*brd*, 10.5)	4.05 (*dd*, 11.5, 2.0)	4.64 (*dd*, 12.0, 2.5)	4.65 (*dd*, 12.0, 2.5)
	3.63 (*dd*, 11.0, 6.0)	3.62 (*dd*, 11.0, 6.5)	3.62 (*dd*, 11.0, 6.5)	3.61 (*dd*, 11.0, 6.5)	3.63 (*dd*, 10.5, 7.5)	3.64 (*dd*, 11.5, 7.5)	4.41 (*dd*, 12.0, 7.5)	4.44 (*dd*, 12.0, 7.5)
Api-1	5.01 (*d*, 2.0)	5.02 (*d*, 2.0)	5.01 (*d*, 2.0)	5.00 (*d*, 2.0)	5.01 (*d*, 2.0)	5.02 (*d*, 2.0)	–	–
-2	3.95 (*d*, 2.0)	4.02 (*d*, 2.0)	4.00 (*d*, 2.0)	4.00 (*d*, 2.0)	4.04 (*d*, 2.0)	4.09 (*d*, 2.0)	–	–
-4	4.08 (*d*, 10.0)	4.09 (*d*, 10.0)	4.06 (*d*, 10.0)	4.07 (*d*, 10.0)	4.17 (*d*, 10.0)	4.21 (*d*, 10.0)	–	–
	3.85 (*d*, 10.0)	3.87 (*d*, 10.0)	3.85 (*d*, 10.5)	3.86 (*d*, 10.0)	3.88 (*d*, 10.0)	3.88 (*d*, 10.0)	–	–
-5	4.37 (*d*, 11.5)	4.40 (*d*, 11.0)	4.37 (*d*, 11.5)	4.38 (*d*, 11.5)	4.37 (*d*, 12.0)	4.37 (*d*, 11.5)	–	–
	4.32 (*d*, 11.5)	4.35 (*d*, 11.0)	4.33 (*d*, 11.5)	4.34 (*d*, 11.5)	4.34 (*d*, 12.0)	4.35 (*d*, 11.5)	–	–
Ester moieties								
-3″	7.57 (*d*, 2.0)	7.57 (*d*, 2.0)	7.56 (*d*, 2.0)	7.54 (*d*, 2.0)	7.52 (*d*, 2.0)	7.30 (*s*)	7.96 (*d*, 8.0)	7.53 (*d*, 2.0)
-4″	–	–	–	–	–	–	6.97 (*d*, 8.0)	–
-6″	7.00 (*d*, 8.5)	7.01 (*d*, 8.0)	7.01 (*d*, 8.0)	6.96 (*d*, 8.5)	6.97 (*d*, 8.5)	–	6.97 (*d*, 8.0)	7.00 (*d*, 8.0)
-7″	7.68 (*dd*, 8.5, 2.0)	7.71 (*dd*, 8.0, 2.0)	7.69 (*dd*, 8.0, 2.0)	7.68 (*dd*, 8.5, 2.0)	7.66 (*dd*, 8.5, 2.0)	7.30 (*s*)	7.96 (*d*, 8.0)	7.68 (*dd*, 8.0 2.0)
—OMes	3.89 (*s*)	3.88 (*s*)	3.88 (*s*)	3.85 (*s*)	3.88 (*s*)	3.84 (*s*)x2	3.86 (*s*)	3.89 (*s*)
	3.85 (*s*)	3.84 (*s*)	3.86 (*s*)	3.80 (*s*)	3.82 (*s*)	3.81 (*s*)	–	3.82 (*s*)

Measured in MeOH-d_4 solution at 35 °C.

[a] Overlapping with other signals.

6.64 (1H, *dd*, J = 8.5, 2.5 Hz, H-6), 3.77 (3H, *s*, –OMe), 3.71 (3H, *s*, –OMe).

Compound **9**: Amorphous powder. $[\alpha]_D^{22}$ –72.0° (MeOH; *c* 1.89). UV λ_{max}^{MeOH} nm (log ε): 201 (4.88), 219 (4.41), 261 (4.07), 286 (3.88). FABMS *m/z*: 635 $[M+Na]^+$, HR-FABMS *m/z*: 635.1951 (Calcd. for $C_{28}H_{36}O_{15}Na$: 635.1952). For ^{13}C and ^{1}H NMR spectra, see Tables 1 and 2. The ^{1}H NMR spectrum of the aglycone moiety was in good agreement with that of **8**.

Compound **10**: Amorphous powder. $[\alpha]_D^{22}$ –75° (MeOH; *c* 0.66). UV λ_{max}^{MeOH} nm (log ε): 202 (4.88), 258 (4.15). FABMS *m/z*: 591 $[M+Na]^+$, HR-FABMS *m/z*: 591.1661 (Calcd. for $C_{26}H_{32}O_{14}Na$: 591.1689). For ^{13}C and ^{1}H NMR spectra, see Tables 1 and 2. The ^{1}H NMR spectrum of the aglycone moiety was in good agreement with that of **8**.

Compound **11**: Amorphous powder. $[\alpha]_D^{22}$ –79.1° (MeOH; *c* 2.05). UV λ_{max}^{MeOH} nm (log ε): 203 (4.97), 256 (4.20). FABMS *m/z*: 635 $[M+Na]^+$, HR-FABMS *m/z*: 635.1929 (Calcd. for $C_{28}H_{36}O_{15}Na$: 635.1952). For ^{13}C and ^{1}H NMR spectra, see Tables 1 and 2. ^{1}H NMR spectrum of the aglycone moiety: δ 6.43 (2H, *s*, H-2, -6), 3.77 (6H, *s*, –OMes), 3.68 (3H, *s*, –OMe).

Compound **12**: Amorphous powder. $[\alpha]_D^{22}$ –78° (MeOH; *c* 0.76). UV λ_{max}^{MeOH} nm (log ε): 203 (5.00), 213 (sh), 261 (4.08), 291 (3.76). FABMS *m/z*: 643 $[M+H]^+$, 665 $[M+Na]^+$, HR-FABMS *m/z*: 643.2223, 665.2051 (Calcd. for $C_{29}H_{39}O_{16}$: 643.2238, $C_{29}H_{38}O_{16}Na$: 665.2057). For ^{13}C and ^{1}H NMR spectra, see Tables 1 and 2. The ^{1}H NMR spectrum of the aglycone moiety was in good agreement with that of **11**.

Compound **13**: Amorphous powder. $[\alpha]_D^{25}$ –83° (MeOH; *c* 0.39). UV λ_{max}^{MeOH} nm (log ε): 203 (4.48), 220 (4.49), 261 (4.19), 287 (3.92). FABMS *m/z*: 605 $[M+Na]^+$, HR-FABMS *m/z*: 605.1817 (Calcd. for $C_{27}H_{34}O_{14}Na$: 605.1846). For ^{13}C and ^{1}H NMR spectra, see Tables 1 and 2. ^{1}H NMR spectrum of the aglycone moiety: δ 6.99 (2H, *d*, J = 9.0 Hz, H-2, -6), 6.75 (2H, *d*, J = 9.0 Hz, H-3, -5), 3.67 (3H, *s*, —OMe).

Compound **14**: Amorphous powder. $[\alpha]_D^{23}$ –74° (MeOH; *c* 0.43). UV λ_{max}^{MeOH} nm (log ε): 202 (4.76), 218 (4.53), 261 (4.18), 286 (4.00). FABMS *m/z*: 635 $[M+Na]^+$, HR-FABMS *m/z*: 635.1924 (Calcd. for $C_{28}H_{36}O_{15}Na$: 635.1952). For ^{13}C and ^{1}H NMR spectra, see Tables 1 and 2. ^{1}H NMR spectrum of the aglycone moiety: δ 7.04 (1H, *d*, J = 9.0 Hz, H-6), 6.52 (1H, *d*, J = 2.5 Hz, H-3), 6.33 (1H, *dd*, J = 9.0, 2.5 Hz, H-5), 3.80 (3H, *s*, –OMe), 3.68 (3H, *s*, —OMe).

Compound **15**: Amorphous powder. $[\alpha]_D^{22}$ –61° (MeOH; *c* 0.79). UV λ_{max}^{MeOH} nm (log ε): 203 (5.07), 212 (sh), 259 (4.48), 289 (sh). FABMS *m/z*: 755 $[M+Na]^+$, HR-FABMS *m/z*: 755.2161 (Calcd. for $C_{35}H_{40}O_{17}Na$: 755.2163). For ^{13}C and ^{1}H NMR spectra, see Tables 1 and 2. ^{1}H NMR spectrum of the aglycone moiety: δ 7.85 (2H, *br d*, J = 8.5 Hz, H-3′, -7′), 7.12 (1H, *d*, J = 8.0 Hz, H-6), 7.03 (1H, *d*, J = 2.0 Hz, H-3), 6.88 (1H, *dd*, J = 8.0, 2.0 Hz, H-5), 6.80 (2H, *br d*, J = 8.5 Hz, H-4′, -6′), 5.13 (2H, *s*, H-α), 3.84 (3H, *s*, —OMe).

Compound **16**: Amorphous powder. $[\alpha]_D^{22}$ –94.8° (MeOH; *c* 1.59). UV λ_{max}^{MeOH} nm (log ε): 201 (4.87), 215 (4.57), 261 (4.29), 296 (3.91). FABMS *m/z*: 653 $[M+H]^+$, 675 $[M+Na]^+$, HR-FABMS *m/z*: 653.2086, 675.1887 (Calcd. for $C_{30}H_{37}O_{16}$: 653.2082, $C_{30}H_{36}O_{16}Na$: 675.1887). For ^{13}C and ^{1}H NMR spectra, see Tables 1 and 2. ^{1}H NMR spectrum of the aglycone moiety: δ 6.51 (1H, *d*, J = 2.5 Hz, H-7), 6.39 (1H, *d*, J = 2.5 Hz, H-5), 4.59 (1H, *m*, H-3), 2.86 (1H, *dd*, J = 16.0, 4.0 Hz, H-4), 2.79 (1H, *dd*, J = 16.0, 10.5 Hz, H-4), 1.42 (3H, *d*, J = 6.5 Hz, H-11).

Compound **17**: Amorphous powder. $[\alpha]_D^{24}$ –95° (MeOH; *c* 0.40). UV λ_{max}^{MeOH} nm (log ε): 213 (4.77), 262 (4.40), 295 (sh). FABMS *m/z*: 705 $[M+Na]^+$, HR-FABMS *m/z*: 705.1976 (Calcd. for $C_{31}H_{38}O_{17}Na$: 705.2007). For ^{13}C and ^{1}H NMR spectra, see Tables 1 and 2. The ^{1}H NMR spectrum of the aglycone moiety was in good agreement with that of **16**.

Compound **18**: Amorphous powder. $[\alpha]_D^{22}$ –35° (MeOH; *c* 0.63). UV λ_{max}^{MeOH} nm (log ε): 203 (5.01), 226 (4.16), 257 (4.18). FABMS *m/z*: 659 $[M+H]^+$, 681 $[M+Na]^+$, HR-FABMS *m/z*: 659.2684, 681.2493 (Calcd. for $C_{34}H_{43}O_{13}$: 659.2704, $C_{34}H_{42}O_{13}Na$: 681.2523). ^{13}C NMR (MeOH-d_4 at 35 °C): δ 167.7 (C-1″), 165.3 (C-5″), 150.5 (C-3), 148.8 (C-3′), 145.9 (C-4), 145.5 (C-4′), 137.4 (C-1), 133.8 (C-1′), 132.8 × 2 (C-3″, -7″), 123.5 (C-2″), 122.8, 122.7 (C-6, -6′), 117.7 (C-5), 115.8 (C-5′), 114.9 × 2 (C-4″, -6″), 114.5 (C-2), 113.4 (C-2′), 102.8 (C_{Glc}-1), 77.9 (C_{Glc}-3), 75.6 (C_{Glc}-5), 74.9 (C_{Glc}-2), 72.1 (C_{Glc}-4), 65.1 (C_{Glc}-6), 62.2 × 2 (C-9, -9′), 56.6, 56.4 (C-3–OMe, -3′–OMe), 56.1 (C-5′–OMe), 44.1 × 2 (C-8, -8′), 36.3, 36.2 (C-7, -7′). ^{1}H NMR: shown in Table 2. The ^{1}H NMR spectral data of the aglycone moiety (MeOH-d_4 at 35 °C): δ 6.90 (1H, *d*, J = 8.0 Hz, H-5), 6.65 (1H, *d*, J = 2.0 Hz, H-2), 6.65 (1H, *d*, J = 8.0 Hz, H-5′), 6.52 (1H, *d*, J = 2.0 Hz, H-2′), 6.52 (1H, *dd*, J = 8.0, 2.0 Hz, H-6′), 6.39 (1H, *dd*, J = 8.0, 2.0 Hz, H-6), 3.74 (3H, *s*, C-3–OMe), 3.69 (3H, *s*, C-3′–OMe), 3.58 (4H, *d*, J = 5.0Hz, H-9, -9′), 2.66 (1H, *dd*, J = 13.5, 6.5 Hz, H-7), 2.64 (1H, *dd*, J = 13.5, 6.5 Hz, H-7′), 2.54 (1H, *dd*, J = 13.5, 8.0 Hz, H-7), 2.52 (1H, *dd*, J = 13.5, 8.0 Hz, H-7′), 1.85 (2H, *m*, H-8, -8′).

Compound **19**: Amorphous powder. $[\alpha]_D^{24}$ –43° (MeOH; *c* 0.49). UV λ_{max}^{MeOH} nm (log ε): 203 (4.99), 219 (4.56), 262 (4.15), 280 (sh). FABMS *m/z*: 711 $[M+Na]^+$, HR-FABMS *m/z*: 711.2609 (Calcd. for $C_{35}H_{44}O_{14}Na$: 711.2629). ^{13}C NMR (MeOH-d_4 at 35 °C): δ 167.7 (C-1″), 155.0 (C-5″), 150.5 (C-3), 150.2 (C-4″), 145.9 (C-4), 145.6 (C-4′), 137.4 (C-1), 133.8 (C-1′), 125.1 (C- 7″), 123.7 (C-2″), 122.8, 122.6 (C-6, -6′), 117.7 (C-5), 115.8 (C-5′), 114.5 (C-2), 113.9 (C-3″), 113.4 (C-2′), 112.1 (C-6″), 102.9 (C_{Glc}-1), 77.8 (C_{Glc}-3), 75.6 (C_{Glc}-5), 75.0 (C_{Glc}-2), 72.1 (C_{Glc}-4), 65.2 (C_{Glc}-6), 62.2 × 2 (C-9, -9′), 56.6 × 3, 56.4 (C-3–OMe, -3′–OMe, -4″–OMe, -5″–OMe), 44.1 × 2 (C-8, -8′), 36.2 × 2 (C-7, -7′). ^{1}H NMR: shown in Table 2. The ^{1}H NMR spectral data of the aglycone moiety (MeOH-d_4 at 35 °C): δ 6.90 (1H, *d*, $J = 8.0$ Hz, H-5), 6.65 (1H, *d*, $J = 2.0$ Hz, H-2), 6.65 (1H, *d*, $J = 8.0$ Hz, H-5′), 6.53 (1H, *br s*, H-2′), 6.52 (1H, *dd*, $J = 8.0, 2.0$ Hz, H-6′), 6.33 (1H, *dd*, $J = 8.0, 2.0$ Hz, H-6), 3.74 (3H, *s*, C-3–OMe), 3.70 (3H, *s*, C-3′–OMe), 3.57 (4H, *d*, $J = 5.0$Hz, H-9, -9′), 2.64 (1H, *dd*, $J = 13.5, 6.5$ Hz, H-7), 2.63 (1H, *dd*, $J = 13.5, 6.5$ Hz, H-7′), 2.53 (1H, *dd*, $J = 13.5, 8.0$ Hz, H-7), 2.52 (1H, *dd*, $J = 13.5, 8.0$ Hz, H-7′), 1.84 (2H, *m*, H-8, -8′).

3.3. Alkaline hydrolysis of compound 3

Compound **3** (1 mg) in 0.05 M NaOH (100 μl) was treated for 3 h at room temperature with stirring under a N_2 gas atmosphere. The reaction mixture was passed through an Amberlite IR-120B column and the eluate was concentrated to dryness. The residue was partitioned between EtOAc and H_2O. Both layers were concentrated to dryness, and by HPLC analysis, 3,4,5-trimethoxybenzoic acid and ajugol (**1a**) were, respectively, identified on comparison with authentic samples. HPLC conditions: column; YMC-ODS 4.6 mm × 25 cm; flow rate: 1.0 ml/min. 22.5% MeCN + 0.05% trifluoroacetic acid (TFA); R_t, 3,4,5-trimethoxybenzoic acid 16.6 min. 5% MeCN; R_t, ajugol 17.4 min.

3.4. Alkaline hydrolysis of compounds 5, 8 and 11

Compounds **5**, **8** and **11** (ca. 10 mg) were dissolved in 0.05 M NaOH (1 ml) and stirred for 2–3 h at room temperature with stirring under a N_2 gas atmosphere. The reaction mixture was treated the above same way. HPLC analysis of the residue from each EtOAc layer suggested that 3,4-dimethoxybenzoic acid was produced from **5** and 4-methoxybenzoic acid was yielded from **8** and **11**. HPLC conditions: column; YMC-ODS 4.6 mm × 25 cm; flow rate: 1.0 ml/min. 20% MeCN + 0.05% TFA; R_t, 3,4-dimethoxybenzoic acid 15.6 min. 27.5% MeCN + 0.05% TFA; R_t, 4-methoxybenzoic acid 12.4 min. Purification of the residue from each H_2O layer using HPLC (YMC-ODS 10 mm × 25 cm, 7.5% MeCN in water) afforded osmanthuside H (**5a**, 5 mg), **8a** (6 mg) and 3,4,5-trimethoxyphenyl 1-*O*-β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside (**11a**, 5 mg). Compounds **5a** and **11a** were identified on comparison of the ^{1}H and ^{13}C NMR spectral data with the reported ones (Sugiyama and Kikuchi, 1993; Kanchanapoom et al., 2002).

Compound **8a** (ca. 0.5 mg) was dissolved in dioxane and 2 M HCl (50 μl each). The solution was heated at 100 °C for 1 h, and the reaction mixture was partitioned between EtOAc and H_2O. By HPLC analysis, 3,4-dimethoxyphenol was detected from the EtOAc layer of compound **8a**. HPLC conditions: column; YMC-ODS 4.6 mm × 25 cm; flow rate: 1.0 ml/min. 20% MeCN; R_t, 3,4-dimethoxyphenol 10.0 min. The H_2O layer was passed through an Amberlite IRA-60E column. The eluate was concentrated to dryness and the residue was stirred with D-cysteine methyl ester hydrochloride, hexamethyldisilazane and trimethylsilylchloride in pyridine using the same procedures as in previous reports (Hara et al., 1987; Zhang et al., 1996). After the reactions, the supernatant was subjected to GC analysis. GC conditions: column; GL capillary column TC-1 (GL Science, Inc.) 0.25 mm × 30 m, Carrier gas N_2, column temperature 230 °C; R_t, D-glucose 21.6 min, L-glucose 20.8 min. D-glucose was detected from compound **8a**.

On the other hand, **8a** being dissolved in dioxane and 2 M HCl was heated at 100 °C for 5 min. The procedures following hydrolysis were the same as described above. The neutralized H_2O layer was reduced with $NaBH_4$ (ca. 1 mg) for 1 h at room temperature. The procedures to alditol acetate were described in previous paper (Nagatani et al., 2001). Apiitol acetate was detected from **8a** by GC analysis. GC conditions: column; Supelco SP-2380^{TM} capillary column 0.25 mm × 30 m, Carrier gas N_2, column temperature 250 °C; R_t, apiitol acetate 8.1 min.

Compound **8a**: Amorphous powder. $[\alpha]_D^{24}$ −113° (MeOH; *c* 0.52,). UV λ_{max}^{MeOH} nm (log ε): 202 (4.48), 223 (3.92), 281 (3.53). FABMS *m/z*: 471 $[M + Na]^+$, HR-FABMS *m/z*: 471.1475 (Calcd. for $C_{19}H_{28}O_{12}Na$: 471.1478). ^{13}C NMR (MeOH-d_4 at 35 °C): δ 153.9 (C-1), 151.2 (C-3), 146.3 (C-4), 114.2 (C-5), 111.0 (C_{Api}-1), 109.6 (C-6), 104.5 (C-2), 103.5 (C_{Glc}-1), 80.5 (C_{Api}-3), 78.0 × 2 (C_{Glc}-3, C_{Api}-2), 77.0 (C_{Glc}-5), 75.0 × 2 (C_{Glc}-2, C_{Api}-4), 71.7 (C_{Glc}-4), 68.8 (C_{Glc}-6), 65.6 (C_{Api}-5), 57.2, 56.6 (C-3–OMe, -4–OMe). ^{1}H NMR (MeOH-d_4 at 35 °C): δ 6.87 (1H, *d*, $J = 8.5$ Hz, H-5), 6.78 (1H, *d*, $J = 2.5$ Hz, H-2), 6.69 (1H, *dd*, $J = 8.5, 2.5$ Hz, H-6), 4.98 (1H, *d*, $J = 2.0$ Hz, H_{Api}-1), 4.74 (overlapping, H_{Glc}-1), 4.02 (1H, *dd*, $J = 11.5, 2.0$ Hz, H_{Glc}-6), 3.96 (1H, *d*, $J = 10.0$ Hz, H_{Api}-4), 3.90 (1H, *d*, $J = 2.0$ Hz, H_{Api}-2), 3.82 (3H, *s*, C-3–OMe), 3.78 (3H, *s*, C-4–OMe), 3.75 (1H, *d*, $J = 10.0$ Hz, H_{Api}-4), 3.62 (1H, *dd*, $J = 11.5, 6.5$ Hz, H_{Glc}-6), 3.57 (2H, *s*, H_{Api}-5), 3.55 (1H, *m*, H_{Glc}-5), 3.42 (overlapping, H_{Glc}-2, H_{Glc}-3), 3.33 (overlapping, H_{Glc}-4).

3.5. Acid hydrolysis of compound 16

Compound **16** (10 mg) was dissolved in 0.2 M HCl (750 μl) and dioxane (300 μl), and heated at 95 °C for 5 h. The reaction mixture was diluted with H_2O and extracted with EtOAc. The EtOAc layer was dried (Na_2SO_4) overnight, the Na_2SO_4 removed by filtration, and the EtOAc evaporated in vacuo to give a residue. The latter was subjected to HPLC (YMC-ODS 10 mm × 25 cm, 27.5% MeCN in water), to afford (−)-6-hydroxymellein **16a** (0.5 mg); the latter being identified on the basis of its ^{1}H NMR (Breinholt et al., 1993), CD spectral data (Antus et al., 1983; Venkatasubbaiah and Chilton, 1991) and optical rotation value (Breinholt et al., 1993).

Compound **16a**: $[\alpha]_D^{24}$ – 33° (MeOH; *c* 0.05)(lit. $[\alpha]_D^{22}$ –57° (MeOH; *c* 0.07)). ^{1}H NMR ($CDCl_3$): δ 11.20 (1H, *br s*, -OH), 6.31 (1H, *br d*, $J = 2.0$ Hz, H-5 or -7), 6.20 (1H, *br s*, H-5 or -7), 4.67 (1H, *m*, H-3), 2.86 (2H, overlapping, H-4), 1.51 (3H, *d*, $J = 6.5$ Hz, H-11). CD$\Delta\varepsilon$ (nm): –2.0 (232), +0.24 (248), −1.4 (268), +0.13 (302) (MeOH; *c* .05)(lit. CD $\Delta\varepsilon$ (nm): −2.4 (195), −2.64 (232), +0.83 (246), −2.96 (268), +0.39 (302) (MeCN)).

3.6. Alkaline hydrolysis of compound 18

Compound **18** (ca. 5 mg) was dissolved in 0.1 M NaOH (1.4 ml) and stirred for 4.5 h at room temperature with stirring under N_2. The reaction mixture was passed through an Amberlite IR-120B column with the eluate concentrated to dryness. The residue was partitioned between EtOAc and H_2O. Both layers were concentrated to dryness, with purification of this solubles HPLC (YMC-ODS 10 mm × 25 cm, 15% MeCN in water) to afford secoisolariciresinol 4-*O*-β-D-glucopyranoside (**18a**, 2 mg) identified on basis its ^{1}H and ^{13}C NMR spectral data. Optical rotation value ($[\alpha]_D^{25}$ –52° (MeOH; *c* 0.16)); (lit. $[\alpha]_D^{25}$ –182.1° (MeOH; *c* 0.05)) (Yuan et al., 2002), Next, 4-methoxybenzoic acid was detected from the residue of the H_2O layer on comparison with authentic sample by HPLC analysis. (Conditions of HPLC analysis were described above.) A part of **18a** (ca. 0.5 mg) was hydrolyzed with 2 M HCl, and D-glucose was detected by GC analysis. (Conditions of GC analysis were described above.)

3.7. Alkaline and acid hydrolysis of compounds 6, 7, 9, 10, 12–17 and 19

Compounds **6**, **7**, **9**, **10**, **12**–**17** and **19** (ca. 0.5 mg) were individually dissolved in 0.05 M NaOH, and stirred for 2 h at room temperature under N_2. The procedures after alkaline hydrolysis were carried out as described above. 4-Hydroxybenzoic acid was detected from the residue of the EtOAc layer derives from compounds **10** and **15** by HPLC analysis. Similarly, HPLC analysis detected 4-methoxybenzoic acid from **6**, 3,4-dimethoxybenzoic acid from **9**, **12**–**16** and **19**, and 3,4,5-trimethoxybenzoic acid from **7** and **17**, respectively. (Conditions of HPLC analysis were described above.) Additionally, 2-(4-hydroxyphenyl)ethyl 1-*O*-β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside (**5a**) was identified from the residues of the H_2O layer of compounds **6** and **7** by HPLC analysis. In the same way, 3,4-dimethoxyphenyl 1-*O*-β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside (**8a**) was detected from **9** and **10**, and 3,4,5-trimethoxyphenyl 1-*O*-β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside (**11a**) and secoisolariciresinol 4-*O*-β-D-glucopyranoside (**18a**) were from **12** and **19**, respectively. HPLC conditions: column; YMC-ODS 4.6 mm × 25 cm; flow rate: 1.0 ml/min. 10% MeCN in water; R_t, **5a** 10.4 min, **8a** 10.2 min, **11a** 15.6 min, 15% MeCN in water; R_t, **18a** 14.4 min.

The residues of H_2O layer of compounds **13**–**17** were hydrolyzed with 2 M HCl and dioxane (50 μl each). The following procedures were described above. By HPLC analysis, 4-methoxyphenol, vanillyl alcohol and (−)-6-hydroxymellein were detected from the residues of the EtOAc layer of compounds **13**, **15** and **17**, respectively. YMC-ODS 4.6 mm × 25 c; flow rate: 1.0 ml/min. 17.5% MeCN in water; R_t, 4-methoxyphenol 17.2 min, 10% MeCN in water; R_t, vanillyl alcohol 10.4 min, 27.5% MeCN in water; R_t, (−)-6-hydroxymellein 15.6 min. D-glucose and apiitol acetate were detected from compounds **13**, **15** and **17** by GC analysis. (Conditions of GC analysis were described above.)

References

Antus, S., Snatzke, G., Steinke, I., 1983. Circular Dichroism, LXXXI. – Synthesis and circular dichroism of steroids with an isochromanone chromophore. Liebigs Ann. Chem. 1983, 2247–2261.

Breinholt, J., Jensen, G.W., Nielsen, R.I., Olsen, E.C., Frisvad, J.C., 1993. Antifungal macrocyclic polylactones from *Penicillium verruculosum*. J. Antibiotics 46, 1101–1108.

Hara, S., Okabe, H., Mihashi, K., 1987. Gas-liquid chromatographic separation of aldose enontiomers as trimethylsilyl ethers of methyl 2-(polyhydroxyalkyl)-thiazolidine-4(*R*)-caroxylate. Chem. Pharm. Bull. 35, 501–506.

Hashimoto, G. Illustrated Cyclopedia of Brazilian Medical Plants. Aboc-sha: Kamakura; 1996, p. 158.

Kanchanapoom, T., Kasai, R., Yamasaki, K., 2002. Iridoid and phenolic glycosides from *Morinda coreia*. Phytochemistry 59, 551–556.

Nagatani, Y., Warashina, T., Noro, T., 2001. Studies on the constituents from the aerial part of *Baccharis dracunculifolia* DC. Chem. Pharm. Bull. 49, 1388–1394.

Nakano, K., Maruyama, K., Murakami, K., Takeishi, Y., Tomimori, T., 1993. Iridoids from *Tabebuia avellanedae*. Phytochemistry 32, 371–373.

Opitz, M., Pachaly, P., Sin, K.S., 1999. New polar ingredients from *Asiasarum sieboldii*. Pharmazie 54, 218–233.

Sugiyama, M., Kikuchi, M., 1993. Phenylethanoid glycosides from *Osmanthus asiaticus*. Phytochemistry 32, 1553–1555.

Venkatasubbaiah, P., Chilton, W.S., 1991. Toxins produced by the dogwood anthracnose fungus *Discula* sp. J. Nat. Prod. 54, 1293–1297.

Yuan, Z., Tezuka, Y., Fan, W., Kanda, S., Li, X., 2002. Constituents of underground parts of *Glehnia littoralis*. Chem. Pharm. Bull. 50, 73–77.

Zhang, D., Miyase, T., Kuroyanagi, M., Umehara, K., Ueno, A., 1996. Studies on the constituents of *Polygala japonica* HOUTT. III. Structures of polygarasaponins XX–XXVII. Chem. Pharm. Bull. 44, 173–179.