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Iridoid and phenolic glycosides from *Morinda coreia*

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Abstract

From the leaves and branches of *Morinda coreia*, six compounds [yopaaosides A–C, 10-*O*-acetylmonotropein, 6-*O*-acetylscandoside and 3,4,5-trimethoxyphenyl 1-*O*-β-apiofuranosyl (1″→6′)-β-glucopyranoside] have been isolated together with five known compounds. Structural elucidations were based on analyses of physical and spectroscopic data. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: *Morinda coreia*; Rubiaceae; Iridoid glucoside; Phenolic glycoside; Yopaaosides A–C; 10-*O*-Acetylmonotropein; 6-*O*-Acetylscandoside

1. Introduction

As part of our ongoing study on Thai medicinal plants, we investigated the constituents of *Morinda coreia* Ham. (Rubiaceae, Thai name: Yo-Paa) collected in the Botanical gardens, Faculty of Pharmaceutical Sciences, Khon Kaen University, Thailand. *M. coreia* is a tree distributed in the south-east Asia region. The bark and wood are used for anti-fever treatments, as well as an antimalarial agent in north-eastern Thai (Isarn) traditional medicine. No phytochemical investigation has been carried out on this species. The present study deals with the isolation and structural elucidation of five new iridoid glucosides (**1**–**5**), and one new phenolic glycoside (**10**), along with the known iridoid glucosides (**6**–**8**), the secoiridoid glucoside (**9**), and the anthraquinone glycoside (**11**) from the leaves and branches of this plant.

2. Results and discussion

The methanolic extract of the leaves and branches of *M. coreia* was suspended in H_2O and defatted with Et_2O. The aqueous layer was subjected to a column of highly porous copolymer resin of styrene and divinylbenzene, using H_2O, MeOH and Me_2CO as eluting solvents successively. The fraction eluted with MeOH was repeatedly subjected to silica gel column chromatography, then RP-18, or prep. HPLC-ODS to afford 11 compounds (**1–11**). Five were identified as the known compounds; asperulosidic acid (**6**), deacetyl-asperuloside (**7**), asperuloside (**8**) (Otsuka et al., 1991), secoxyloganin (**9**) (Calis and Sticher, 1984), and lucidine 3-*O*-β-primeveroside (**11**) (Lu et al., 1998) by the physical data and spectroscopic evidence.

The molecular formula of compound **1** was determined as $C_{27}H_{28}O_{15}$ by HR–FAB mass spectrometry. The ^1H and ^{13}C NMR spectral data revealed the presence of an iridoid skeleton with a β-glucopyranosyl unit and a carbomethoxy group at C-4. The chemical shifts of two methine carbons at δ 58.0 and 59.2 were assigned as an epoxy group on C-6 and C-7 of the cyclopentanopyran ring. The quaternary carbons at δ 92.7 (C-8), 169.3 (C-12), 133.9 (C-11), as well as a methine carbon at δ156.2 (C-10) were very characteristic for a spiro-lactone ring at C-8, corresponding to a plumieride type iridoid (Yamauchi et al., 1981). In addition, the signals of a 1,3,4-trisubstituted aromatic ring, one methoxy group and one carbonyl carbon were observed. Based on the HMBC analysis, the additional unit was assigned to be attached at C-11 (δ 133.9) of a spiro-lactone ring, in which H-10 (δ 7.56, *s*), H-2″ (δ 7.42) and H-6″ (δ 7.45) exhibited a three-bond correlation with C-13 (δ 187.7; Table 1). The methoxyl group of the additional unit was then located at C-3″ by a difference NOE experiment in

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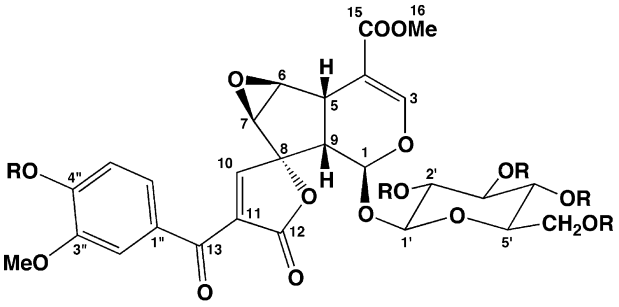
Table 1
NMR spectral data of compounds **1** and **2** (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR)

No.	**1**			**2**		
	^{1}H NMR	^{13}C NMR	HMBC	^{1}H NMR	^{13}C NMR	HMBC
1	5.60 (1H, *bs*)	92.7	3, 5, 1′	5.35 (1H, *bs*)	92.8	3, 5, 8, 1′
3	7.51 (1H, *d*, *J* = 1.5 Hz)	153.6	1, 4, 15	7.43 (1H, *d*, *J* = 1.7 Hz)	153.3	1, 4
4		108.5			108.0	
5	3.46 (1H, *bd*, *J* = 8.3 Hz)	33.1	1, 3, 8	3.37 (1H, *dd*, *J* = 8.5, 1.7 Hz)	33.2	1, 8
6	4.02 (1H, *d*, *J* = 2.5 Hz)	58.0	8, 9	4.04 (1H, *d*, *J* = 2.4 Hz)	58.1	8, 9
7	3.50 (1H, *d*, *J* = 2.5 Hz)	59.2	6, 8, 9	3.83 (1H, *d*, *J* = 2.4 Hz)	58.2	8, 9
8		92.7			92.6	
9	2.85 (1H, *dd*, *J* = 8.3, 1.2 Hz)	44.2	1, 4, 5, 8, 10	2.45 (1H, *d*, *J* = 8.5 Hz)	45.1	1, 5, 8, 10
10	7.56 (1H, *s*)	156.2	8, 11, 12, 13	5.13 (1H, *d*, *J* = 1.0 Hz)	69.1	8, 9, 11, 12, 13
11		133.9			123.9	
12		169.3			172.7	
13		187.7		7.57 (1H, *d*, *J* = 1.0 Hz)	144.0	11, 12, 2″, 6″
15		167.8			168.0	
16	3.70 (3H, *s*)	52.1	15	3.71 (1H, *s*)	52.0	15
1′	4.51 (1H, *d*, *J* = 7.8 Hz)	99.6	1	4.42 (1H, *d*, *J* = 7.8 Hz)	99.3	1, 3′
2′	3.11 (1H, *dd*, *J* = 8.8, 7.8 Hz)	74.4	1′	3.05 (1H, *dd*, *J* = 9.3, 7.8 Hz)	74.3	
3′	3.30 (1H, *dd*, *J* = 9.5, 8.8 Hz)	77.8		3.23[a] (1H)	77.6	
4′	3.19 (1H, *dd*, *J* = 9.5, 8.6 Hz)	71.5		3.23[a] (1H)	71.1	
5′	3.26 (1H, *m*)	78.5		3.16 (1H, *m*)	77.9	
6′	3.83 (1H, *dd*, *J* = 12.0, 2.0 Hz)	62.7		3.74 (1H, *dd*, *J* = 12.2, 2.2 Hz)		
	3.57 (1H, *dd*, *J* = 12.0, 6.1 Hz)			3.58 (1H, *dd*, *J* = 12.2, 5.4 Hz)	62.3	
1″		129.1			126.2	
2″	7.42 (1H, *d*, *J* = 2.0 Hz)	113.0	13, 3″, 4″	7.61 (1H, *d*, *J* = 8.8 Hz)	134.8	13, 4″
3″		149.2		6.84 (1H, *d*, *J* = 8.8 Hz)	117.0	1″, 4″
4″		154.8			162.1	
5″	6.84 (1H, *d*, *J* = 8.3 Hz)	116.2	4″	6.84 (1H, *d*, *J* = 8.8 Hz)	117.0	
6″	7.45 (1H, *dd*, *J* = 8.3, 2.0 Hz)	126.8	13	7.61 (1H, *d*, *J* = 8.8 Hz)	134.8	
OMe	3.88 (3H, *s*)	56.5				

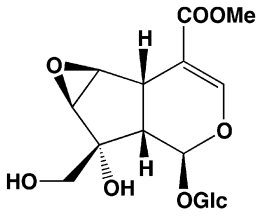
[a] Chemical shifts obtained approximately from COSY and HSQC.

the ^{1}H NMR, and irradiation of this methoxy signal (δ 3.88) caused an NOE enhancement at H-2″ (δ 7.42, *d*, *J* = 2.0 Hz). The epoxide on C-6 and C-7 was assigned to the β-configuration due to the small coupling constant between H-6 and H-5 which can be explained by the expansion of the dihedral angle between these two protons to approximately 90°. Moreover, the chemical shifts of C-6 and C-7 were very similar to a closely related compound, 6β,7β-epoxysplendoside (**1b**) (Jensen and Nielsen, 1982). The relative configuration at C-8 was determined by comparing the chemical shift of its C-9 acetate (**1a**) with the reported data for 6β,7β-epoxysplendoside pentaacetate (Damtoft et al., 1981; Jensen and Nielsen, 1982). The chemical shift found for C-9 of **1a** at δ 42.8 as well as for 6β,7β-epoxysplendoside pentaacetate at δ 42.7, was recorded in $CDCl_3$, indicating that C-10 (δ 156.2) was in a β-position relative to C-8. Furthermore, irradiation of H-1 (δ 5.60) signal gave rise to an NOE enhancement at H-9 (δ 2.85), but no NOE enhancement was observed for H-10 (δ 7.56), confirming the β-position. Besides, a survey of plumieride type iridoid glucosides revealed that the reported α-position of C-10 has a chemical shift at C-9 of by about 50.0 ppm, whereas the chemical shift reported for β-position of C-10 was 46.2 ppm, recorded in CD_3OD or C_5D_5N (Abe et al., 1988; Chaudhuri et al., 1980; Siddiqui et al., 1994). On the basis of these spectral data, the structure of compound **1** was identified as shown, named yopaaoside A.

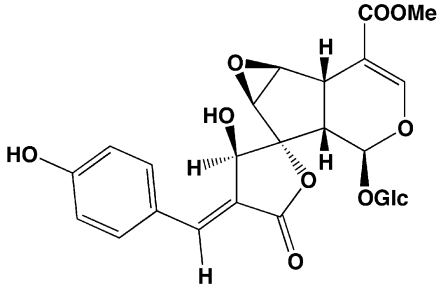
The molecular formula of compound **2** was determined as $C_{26}H_{28}O_{14}$ by HR–FAB mass spectrometry. Compound **2** revealed similar chemical shifts of the cyclopentanopyran ring from the ^{13}C NMR spectrum with those of **1**, indicating the presence of a 6β,7β-epoxy group at C-6 and C-7, a spiro-lactone ring connected at C-8, together with a β-position at C-10. In addition, signals for a *p*-hydroxy aromatic ring, an oxygenated methine, as well as an olefinic methine were observed from analysis of the spectra. The assignments were supported by COSY, HSQC, HMBC and difference NOE experiments. In the HMBC spectrum, the oxygenated proton (δ 5.13), corresponding to δ 69.1 in the ^{13}C NMR spectrum provided significant correlations between C-8 (δ 92.6), C-9 (δ 45.1), C-12 (172.7) and the carbon signals at δ 123.9 and 144.0. Moreover, the olefinic proton (δ 7.57), corresponding to δ 144.0 in the ^{13}C NMR



1 R = H
1a R = Ac



1b



2

spectrum, showed long-range correlations to a carbon signal at δ 123.9 together with C-12 (δ 172.7) and C-2″,6″ (δ 134.8). Therefore, the carbon signals at δ 69.1, 123.9 and 144.0 could be assigned to C-10, C-11 and C-13, respectively, and the *p*-hydroxy aromatic ring was attached to C-13. The *R* configuration of C-10 was assigned by irradiation of the signal at δ 5.13 (H-10) which caused an NOE enhancement only for H-2″,6″ (δ 7.61) but not for H-9 (δ 2.45); this in turn indicated the location of the *p*-hydroxy aromatic ring was at C-13. Accordingly, the structure of compound **2** was elucidated as shown in the formula, named yopaaoside B.

Compound **3** had a molecular formula of $C_{17}H_{26}O_{12}$, as determined from HR-FAB mass spectrometric analysis. The ^{1}H and ^{13}C NMR spectral data revealed the presence of one β-glucopyranosyl unit and an iridoid aglycone together with a carbomethoxy group at C-4. Compound **3** showed the same substituted hydroxyl group patterns as that in nyctanthoside (**3a**), previously

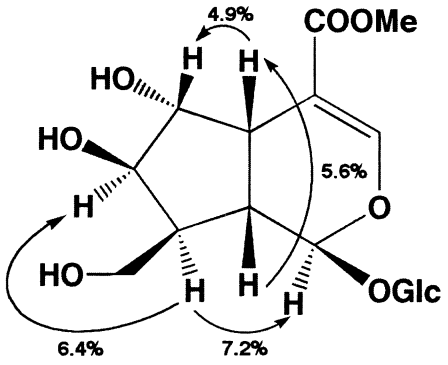


Fig. 1. The significant NOE differences of compound **3**.

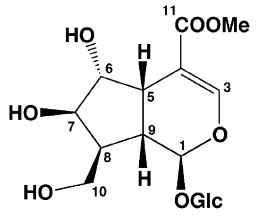
isolated from *Nyctanthes arbor-tristis* (Rimpler and Tunghanns, 1975). However, differences in chemical shifts were observed in the ^{1}H NMR spectrum, indicating the presence of a different relative configuration. The complete assignments were established by analysing the COSY and HSQC spectra, as well as the coupling constants in the ^{1}H NMR spectrum and the chemical shifts in the ^{13}C NMR spectrum. The coupling constant between H-5 and H-6 ($J = 3.4$ Hz) together with the downfield shift of C-1 (δ 102.4) and the calculation of the shift difference between C-3 and C-4 (48.3) indicated that the orientation of the hydroxy group at C-6 was α (Damtoft et al., 1981). The appearance of H-6 as a broad doublet (δ 4.22, $J = 3.4$ Hz) provided a small coupling constant between H-6 and H-7 ($J < 1.0$ Hz) corresponding to a dihedral angle of approximately 90°, which led us to conclude that the hydroxy group at C-7 was in the β-epimer. Also, the appearance of H-7 as a broad doublet (δ 4.05, $J = 4.9$ Hz) revealed a large coupling constant with H-8 (δ 2.32) indicating the α-position of this proton. Moreover, the difference NOE experiments (Fig. 1) confirmed the relative configurations of the hydroxyl groups at C-6 and C-7 were α and β, respectively, and the proton at C-9 was in a β-position. Consequently, the structure of compound **3** was elucidated as shown, named yopaaoside C (Fig. 1).

The molecular formula of compound **4** was determined as $C_{18}H_{24}O_{12}$ by HR-FAB mass spectrometry. The ^{1}H and ^{13}C NMR spectral data revealed the presence of one acetyl group, one β-glucopyranosyl unit and the remaining signals were consistent with an iridoid skeleton. The chemical shifts of **4** were very similar to those reported for monotropein (Davini et al., 1981). However, the C-10 downfield shift (δ 70.6 from δ 67.4) and the C-8 upfield shift (δ 84.1 from δ 85.6) established the attachment of the acetyl group to the C-10 carbon. Consequently, the structure of compound **4** was assigned as 10-*O*-acetylmonotropein.

The molecular formula of compound **5** was determined as $C_{18}H_{24}O_{12}$ by HR-FAB mass spectrometry. The ^{1}H and ^{13}C NMR spectra indicated an iridoid structure. The chemical shifts of **5** coincided with those of scandoside (Chaudhuri et al., 1980) except that an

acetyl group was also observed. The attachment of an acetyl group was assigned to C-6 (δ 83.6) due to the observation of the downfield shift of this signal by 1.3 ppm together with the upfield shifts of C-5 (4.8 ppm) and C-7 (2.9 ppm). Therefore, the structure of compound **5** was 6-*O*-acetylscandoside.

Compound **10** had the molecular formula $C_{20}H_{30}O_{13}$ as deduced from its HR–FAB mass spectrometry. The ^1H and ^{13}C NMR spectra revealed the presence of one 1,3,4,5 tetrasubstituted symmetrical aromatic ring, and one methoxyl and two equivalent methoxyl groups, indicating that compound **10** was an aromatic glycoside. The sugar moiety was identified as β-apiofuranosyl (1″→6′)-β-glucopyranose by comparison of the chemical shifts with the reported data (Zhong et al., 1998). The positions of the two equivalent methoxyl groups were assigned to the C-3 and C-5 positions, as revealed by the difference NOE experiment, in which irradiation of H-1′ (δ 4.79) caused an increase in the NOE enhancement at H-2,6 (δ 6.45). Consequently, the structure of compound **10** was proposed as 3,4,5-trimethoxyphenyl 1-*O*-β-apiofuranosyl (1″→6′)-β-glucopyranoside.



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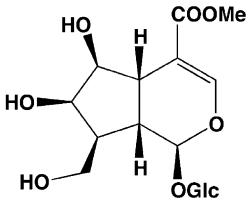
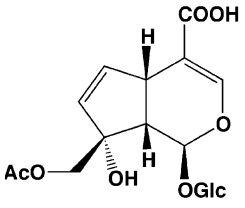


3a



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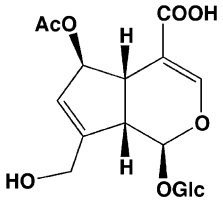

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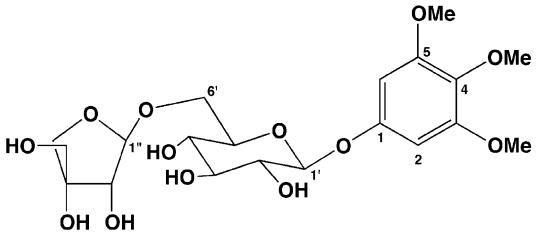

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3. Experimental

3.1. General

NMR spectra were recorded in CD_3OD or $CDCl_3$ using a JEOL JNM A-400 spectrometer (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) with tetramethylsilane (TMS) as internal standard. MS were recorded on a JEOL JMS-SX 102 spectrometer. Preparative HPLC employed ODS columns (150×20 mm i.d., YMC) with a Tosoh refraction index (RI-8) detector and a flow rate of 6 ml/min. For CC, silica gel G 60 (Merck), RP-18 (50 μm, YMC) and highly porous copolymer of styrene and divinylbenzene (Mitsubishi Chem. Ind. Co. Ltd) were used. The solvent systems were: (I) EtOAc–MeOH–H_2O (4:1:0.1); (II) EtOAc–MeOH–H_2O (7:3:0.3); (III) EtOAc–MeOH–H_2O (6:4:1); (IV) 20–60% MeOH in H_2O (V) 10-70% MeOH; in H_2O (VI) 20% MeCN; in H_2O (VII) 5% MeCN; in H_2O (VIII) 10% MeOH in H_2O and (IX) 10% MeCN in H_2O. The spray reagent used was 10% H_2SO_4 in ethanol.

3.2. Plant material

M. coreia was collected in November 2000 from the Botanical Gardens, Faculty of Pharmaceutical Sciences, Khon Kaen University, Thailand. The identification of the plant was confirmed by Professor Vichiara Jirawongse, Department of Pharmaceutical Botany and Pharmacognosy, Faculty of Pharmaceutical Sciences, Khon Kaen University. A voucher sample (KKU-0019) is kept in the Herbarium of the Faculty of Pharmaceutical Sciences, Khon Kaen University, Thailand.

3.3. Extraction and isolation

The dried leaves and branches (2.3 kg) of *M. coreia* were extracted with hot MeOH (reflux at 75 °C, 40 lit.). After removal of the solvent by evaporation, the residue (151.0 g) was defatted with Et_2O. The aqueous layer was subjected to a column of highly porous copolymer of styrene and divinylbenzene and eluted with H_2O, MeOH and Me_2CO, successively. The fraction eluted with MeOH (35.0 g) was subjected to a column of silica gel (systems I, II and III, respectively) affording six fractions. Fraction 2 (5.5 g) was applied to a RP-18 column using system IV to provide 12 fractions together with compound **1** (1.2 g). Fraction 2-4 was purified by prep. HPLC-ODS (system VI) to give compound **2** (95 mg). Fraction 3 (8.2 g) was further separated on a column of RP-18 column (system V) to give 13 fractions. Fraction 3-1 was purified by prep. HPLC-ODS (system VII and VIII) to provide compounds **4** (18 mg) and **5** (71 mg). Fraction 3-2 was similarly purified by prep. HPLC-ODS (system IX) to afford compounds **6** (52 mg) and **10** (8 mg). Compound **8** (3.5 g) was crystallized from fraction 3-3. Fraction 3-4 was purified by prep. HPLC-ODS (system VI) to give compound **9** (111 mg).

Table 2
^{1}H NMR spectral data of compounds **3**–**5** (400 MHz, CD_3OD)

H	3	4	5
1	5.03 (1H, *d*, *J* = 8.8 Hz)	5.64 (1H, *d*, *J* = 2.2 Hz)	5.23 (1H, *d*, *J* = 6.1 Hz)
3	7.58 (1H, *d*, *J* = 1.7 Hz)	7.36 (1H, *d*, *J* = 1.2 Hz)	7.46 (1H, *s*)
5	3.08 (1H, *ddd*, *J* = 9.3, 3.4, 1.7 Hz)	3.28 (1H, *m*)	3.26 (1H, *m*)
6	4.22 (1H, *bd*, *J* = 3.4 Hz)	6.22 (1H, *dd*, *J* = 5.7, 2.2 Hz)	5.56 (1H, *m*)
7	4.05 (1H, *bd*, *J* = 4.9 Hz)	5.60 (1H, *dd*, *J* = 5.7, 2.0 Hz)	5.75 (1H, *bs*)
8	2.32 (1H, *m*)		
9	1.80 (1H, *m*)	2.61 (1H, *dd*, *J* = 8.8, 2.2 Hz)	3.00 (1H, *dd*, *J* = 7.3, 6.4 Hz)
10	3.79[a] (1H)	4.16 (1H, *d*, *J* = 11.2 Hz)	4.32 (1H, *d*, *J* = 15.4 Hz)
	3.75[a] (1H)	4.06 (1H, *d*, *J* = 11.2 Hz)	4.15 (1H, *d*, *J* = 15.4 Hz)
COOMe	3.67 (3H, *s*)		
1′	4.63 (1H, *d*, *J* = 7.8 Hz)	4.62 (1H, *d*, *J* = 7.8 Hz)	4.64 (1H, *d*, *J* = 7.8 Hz)
2′	3.18 (1H, *dd*, *J* = 8.6, 7.8 Hz)	3.16 (1H, *dd*, *J* = 8.8, 7.8 Hz)	3.17 (1H, *dd*, *J* = 8.8, 7.8 Hz)
3′	3.34 (1H, *dd*, *J* = 9.0, 8.6 Hz)	3.31 (1H, *dd*, *J* = 9.3, 8.8 Hz)	3.34 (1H, *dd*, *J* = 9.0, 8.8 Hz)
4′	3.23[a] (1H)	3.23[a] (1H)	3.23[a](1H)
5′	3.23 (1H, *m*)	3.23 (1H, *m*)	3.23 (1H, *m*)
6′	3.80 (1H, *dd*, *J* = 12.2, 2.2 Hz)	3.83 (1H, *bd*, *J* = 11.5 Hz)	3.83 (1H, *dd*, *J* = 12.2, 2.0 Hz)
	3.64 (1H, *dd*, *J* = 12.2, 5.1 Hz)	3.64 (1H, *dd*, *J* = 11.5, 4.9 Hz)	3.60 (1H, *dd*, *J* = 12.2, 5.4 Hz)
OAc		2.05 (3H, *s*)	1.98 (3H, *s*)

[a] Chemical shifts obtained approximately from COSY and HSQC.

Table 3
^{13}C NMR spectral data of compounds **3**–**5** (100 MHz, CD_3OD)

C	3	4	5
1	102.4	94.7	97.7
3	155.7	152.4	154.0
4	107.4	111.0	110.1
5	40.6	39.0	42.1
6	79.3	138.2	83.6
7	77.5	132.7	127.0
8	48.0	84.1	150.3
9	40.5	46.5	46.8
10	62.0	70.6	60.9
11	169.4	170.1	170.1
OMe	51.7		
1′	101.1	99.8	100.2
2′	74.8	74.6	74.7
3′	77.9	78.0	77.8
4′	71.3	71.4	71.4
5′	78.2	78.3	78.3
6′	62.5	62.5	62.6
$CH_3\underline{C}O$		172.8	172.8
$\underline{C}H_3CO$		20.8	21.2

Fraction 4 (4.5 g) was subjected to a column of RP-18 (system V) to provide 14 fractions. Fraction 4-1 was further purified by prep. HPLC-ODS (system VII) to give compounds **3** (9 mg) and **7** (89 mg). Finally, compound **11** (60 mg) was crystallized from fraction 4-10.

3.4. Yopaaoside A (*1*)

Yellow amorphous powder, $[\alpha]_D^{19}$ −19.3° (MeOH, c 2.1); ^{1}H and ^{13}C NMR spectra (CD_3OD; Table 1); Negative HR–FAB–MS, *m*/*z*: 591.1387 ($C_{27}H_{27}O_{15}$ requires 591.1349).

3.5. Acetylation of yopaaoside A (*1*)

Yopaaoside A (60 mg) was acetylated with Ac_2O-pyridine (each 1 ml) at room temperature for 24 h. The reaction mixture was dried under N_2 gas to provide yopaaoside A pentaacetate (**1a**) (75 mg), whose structure was identified by spectral analysis.

3.6. Yopaaoside A pentaacetate (*1a*)

Amorphous powder. ^{1}H NMR ($CDCl_3$): δ 5.35 (1H, *bs*, H-1), δ 7.40 (1H, *d*, *J* = 1.4 Hz, H-3), δ 3.42 (1H, *bd*, *J* = 8.1 Hz, H-5), δ 3.48 (1H, *d*, *J* = 2.5 Hz, H-6), δ 4.12 (1H, *d*, *J* = 2.5 Hz, H-7), δ 3.04 (1H, *bd*, *J* = 8.3 Hz, H-9), δ?7.47 (1H, *s*, H-10), δ 3.78 (3H, *s*, H-16), δ 4.82 (1H, *d*, *J* = 8.1 Hz, H-1′), δ 4.95 (1H, *dd*, *J* = 9.3, 8.3 Hz, H-2′), δ 5.22 (1H, *dd*, *J* = 9.5, 9.5 Hz, H-3′), δ 5.11 (1H, *dd*, *J* = 9.8, 9.5 Hz, H-4′), δ 4.11 (1H, *m*, H-5′), δ 4.31 (1H, *dd*, *J* = 12.7, 4.2 Hz, H-6′), δ 4.11 (1H, *dd*, *J* = 12.7, 2.4 Hz, H-6′ δ 7.56 (1H, *d*, *J* = 1.7 Hz, H-2″ δ 7.16 (1H, *d*, *J* = 8.3 Hz, H-5″ δ 7.38 (1H, *dd*, *J* = 8.3, 1.7 Hz, H-6″ δ 2.35, 2.04, 2.02, 2.00, 1.91 (3H×5, each *s*, 5×CH_3CO); ^{13}C NMR ($CDCl_3$): δ 91.7 (C-1), δ 151.5 (C-3), δ 108.1 (C-4), δ 31.7 (C-5), δ 57.7 (C-6), δ 56.5 (C-7), δ 90.9 (C-8), δ 42.6 (C-9), δ 155.9 (C-10), δ 132.9 (C-11), δ 166.9 (C-12), δ 185.7 (C-13), δ 165.7 (C-15), δ 51.9 (C-16), δ 96.0 (C-1′), δ 70.6 (C-2′), δ 72.2 (C-3′), δ 67.8 (C-4′), δ 72.2 (C-5′), δ 61.4 (C-6′), δ 134.2 (C-1″), δ 112.5 (C-2″), δ 145.1 (C-3″), δ 151.9 (C-4″), δ 123.1 (C-5″), δ 123.5 (C-6″), δ 56.1(MeO-3), δ 170.8, 170.3, 169.4, 168.9, 168.5

(5×$CH_3\underline{C}O$), and δ 20.7, 20.6, 20.6, 20.5, 20.1 (5×$\underline{C}H_3CO$); Negative FAB–MS, *m*/*z*: 801.

3.7. Yopaaoside B (**2**)

Yellow amorphous powder, $[\alpha]_D^{19}$ −66.1 °C (MeOH, *c* 1.6); ^1H and ^{13}C NMR (CD_3OD spectra; Table 1); Negative HR–FAB–MS, *m*/*z*: 563.1390 ($C_{26}H_{27}O_{14}$ requires 563.1400).

3.8. Yopaaoside C (**3**)

Amorphous powder, $[\alpha]_D^{19}$ −128.5 °C (MeOH, *c* 0.6); For ^1H NMR (CD_3OD) and ^{13}C NMR (CD_3OD spectra; Tables 2 and 3); Negative HR–FAB–MS, *m*/*z*: 421.1339 ($C_{17}H_{25}O_{12}$ requires 421.1345).

3.9. 10-O-Acetylmonotropein (**4**)

Amorphous powder, $[\alpha]_D^{19}$ −95.3 °C (MeOH, *c* 1.2); For ^1H NMR (CD_3OD) and ^{13}C NMR (CD_3OD; Tables 2 and 3); Negative HR–FAB–MS, *m*/*z*: 431.1178 ($C_{18}H_{23}O_{12}$ requires 431.1189).

3.10. 6-O-Acetylscandoside (**5**)

Amorphous powder, $[\alpha]_D^{19}$ −82.7 °C (MeOH, *c* 1.2); For ^1H NMR (CD_3OD and ^{13}C NMR (CD_3OD spectra; Tables 2 and 3); Negative HR–FAB–MS, *m*/*z*: 431.1149 ($C_{18}H_{23}O_{12}$ requires 431.1189).

3.11. 3,4,5-Trimethoxyphenyl 1-O-β-apiofuranosyl (1″→6′)-β-glucopyranoside (**10**)

Amorphous powder, $[\alpha]_D^{19}$ −137.5 °C (MeOH, *c* 0.6); ^1H NMR (CD_3OD): δ 6.45 (2H, *s*, H-2,6), δ 3.81 (6H, *s*, MeO-3,5), δ 3.70 (3H, *s*, MeO-4), δ 4.79 (1H, *d*, *J* = 7.3 Hz, H-1′), δ 4.96 (1H, *d*, *J* = 2.5 Hz, H-1″), δ 3.87 (1H, *d*, *J* = 2.5 Hz, H-2″), δ 3.94 (1H, *d*, *J* = 9.8 Hz, H-4″), δ 3.73 (1H, *d*, *J* = 9.8 Hz, H-4″) and δ 3.54 (2H, *s*, H-5″); ^{13}C NMR (CD_3OD): δ 134.6 (C-1), δ 96.4 (C-2,6), δ 154.8 (C-3,5), δ 156.0 (C-4), δ 56.7 (MeO-3,5), δ 61.2 (MeO-4), δ 103.2 (C-1′), δ 74.9 (C-2′), δ 77.9 (C-3′), δ 71.6 (C-4′), δ 77.0 (C-5′), δ 68.8 (C-6′), δ 110.9 (C-1″), δ 77.9 (C-2″), δ 80.5 (C-3″), δ 74.9 (C-4″) and δ 65.4 (C-5″); Negative HR–FAB–MS, *m*/*z*: 477.1580 ($C_{20}H_{29}O_{13}$ requires 477.1607).

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