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TRITERPENOID SAPONINS FROM *DIANTHUS CHINENSIS*

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Key Word Index—*Dianthus chinensis*; Caryophyllaceae; aerial parts; triterpenoid saponins; dianchinenoside C; dianchinenoside D; hainanenside.

Abstract—Two novel triterpenoid saponins, dianchinenoside C [23-*O*-β-D-glucopyranosyl 3β,16α-dihydroxyolean-12-ene 23α, 28β-dioic acid 28-*O*-β-D-glucopyranoside] and dianchinenoside D [3β,16α-dihydroxyolean-12-ene 23α,28β-dioic acid 28-*O*-β-D-glucopyranosyl (1→6)-β-D-glucopyranoside] were isolated from the aerial parts of *Dianthus chinensis*. Their structures were determined by spectroscopic methods and chemical evidence. We also report the revision of a previous misassignment of hainanenside, isolated from *Ilex hainanensis* Merr. In addition, known compounds, 3-*O*-α-L-arabinopyranosyl hederagenin 28-*O*-β-D-glucopyranosyl (1→6)-β-D-glucopyranoside, sitosterol 3β-*O*-β-D-glucopyranoside, isoorientin-2″-*O*-glucoside, isovitexin-2″-*O*-glucoside, and chrysoeriol-7-*O*-glucoside, were also identified.

INTRODUCTION

The genus *Dianthus* (Caryophyllaceae) is widely distributed in China, especially in the northeast district of China. About three species of *Dianthus* have been used in Chinese traditional medicine as a diuretic and antiinflammatory agent [1]. In previous phytochemical studies, saponins [2–7], flavonoids [8–13], a sterol [14] and glycosides [15] have been reported as the main constituents of this genus. More recently, from the aerial parts of *D. chinensis*, we reported the structure elucidation of triterpenoid saponins, dianchinenoside A and B, which were isolated from the *n*-butanol soluble fraction of a 95% aqueous ethanol extract of the herbs of *D. chinensis* [16]. Continuing the search for new saponins of this plant, we have isolated two novel triterpenoid saponins having R_f values close to those of dianchinenoside A and B on TLC, and named them dianchinenoside C (**1**) and dianchinenoside D (**2**). This paper mainly deals with their isolation and structural elucidation. In addition, we also isolated a saponin to which, on the basis of physical data, we assigned structure **3**. A literature search then revealed that the same structure had already been given to a saponin, hainanenside isolated from *Ilex hainanensis* Merr. [17]. However, as some physical data for the two compounds differ from each other (e.g., three resonances differ by *ca* 3–6 ppm in their ^{13}C NMR), the evidence that **3** is indeed the correct structure for our plant material was also described. We also report here the isolation of known compounds, 3-*O*-α-L-arabinopyranosyl hederagenin 28-*O*-β-D-glucopyranosyl (1→6)-β-D-glucopyranoside (**6**), isoorientin-2″-*O*-glucoside (**7**), isovitexin-2″-*O*-glucoside (**8**), chrysoeriol-7-*O*-glucoside (**9**) and sitosterol 3β-*O*-β-D-glucopyranoside (**10**).

RESULTS AND DISCUSSION

A 95% ethanol extract of the dried aerial parts (6 kg) of *D. chinensis* was partitioned between chloroform and water. The aqueous layer was further extracted with ethyl acetate and *n*-butanol, successively. The *n*-butanol and ethyl acetate soluble fractions were chromatographed on Dianion HP-20, Toyopearl HW-40F, polyamide column and silica gel, followed by MPLC and HPLC to afford two minor saponins **1** and **2** along with known compounds.

Dianchinenoside C (**1**), powder, mp 225–227°, $[\alpha]_D^{16}$ +12.4°. It had the molecular formula of $C_{42}H_{66}O_{16}$, established by positive ion FAB mass (at *m/z* 865 $[M+K]^+$ and 849 $[M+Na]^+$) and ^{13}C NMR data. The IR spectrum contained a hydroxyl band at 3402 cm^{-1}, a carboxylic band at 1709 cm^{-1}, and an esteric band at 1734 cm^{-1}. The ^{1}H NMR (Table 1) spectrum showed the signals of six tertiary methyl groups at δ0.97, 0.99, 1.03, 1.16, 1.59, 1.69, one trisubstituted olefinic proton at δ5.43 (*br s*), and two anomeric protons at δ6.29 and 6.39 (*d*, *J* = 8 Hz). ^{13}C NMR (Table 2) spectroscopic data revealed the presence of six sp^3 quaternary carbon atoms at δ30.8, 37.0, 40.5, 42.0, 49.1, 55.3, a pair of olefinic carbon atoms at δ122.7 and 144.6, two anomeric carbon atoms at δ95.9 and 96.5, and two ester carbonyls at δ177.6 and 176.0. The chemical shift of both anomeric carbon signals showed the sugar residues were attached to the aglycone by ester bonds. These spectral data suggested that **1** was a

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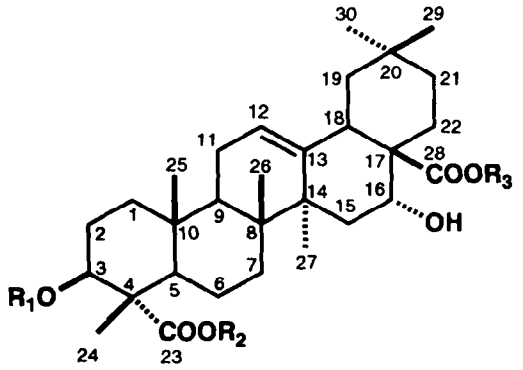

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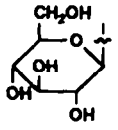
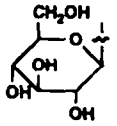
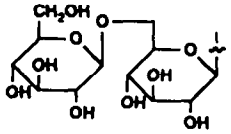
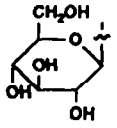
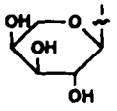
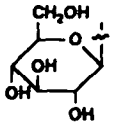
1.	H		
2.	H	H	
3.	H	H	
4.		H	
5.	H	H	H

saponin of an oleanolic-type triterpene. Comparison of the ^1H and ^{13}C NMR spectra of **1** with those of dianchinenoside A (**4**) showed great similarity [16]. Since both the ^1H and ^{13}C NMR spectra exhibited sugar signals, **1** was subjected to acid hydrolysis with 1M HCl to yield sugar components identified as D-glucose by GLC as its TMSi derivative. Moreover, the FAB mass spectrum of **1** showed ions at *m/z* 687 $[M+Na-162]^+$ due to loss of one glucose unit, and the fragment at *m/z* 503 $[M+H-324]^+$ arising from the loss of two glucose units, which supported hydrolysis results. The modes of both glycoside linkages of the glucose unit were regarded as β from the ^1H–^1H coupling anomeric proton constants of 8 Hz. The 2D NMR provided further insights into the structure. The ^1H–^1H COSY spectrum showed coupling interaction between the proton δ2.47 (15-ax), 1.66 (15-eq) and 5.22 (H-16), which assigned a hydroxyl group to the 16 position. The ^1H–^{13}C COSY spectrum showed a strong cross-peak at δ75.1/4.66 indicating that the protons resonating at δ4.66 (H-3) are attached to the carbon resonating at δ75.1 (C-3). Another strong peak linking the signal of H-16 at δ5.22 with the signal of C-16 at δ74.4 was observed, which confirmed the assignment of the 16-hydroxyl group. The anomeric carbon atoms at δ95.9 and 96.5 were coupled to the anomeric protons at δ6.29 and 6.39, and the C-2, C-12 and C18 were coupled to the protons at δ1.91, 5.43 and 3.50, respectively. These 2D NMR data were reminiscent of the aglycone of **1** which was identical with that of **4**. The aglycone structure of **1** was further confirmed by acid hydrolysis. Hydrolysis with 1M HCl afforded **5**, which has been elucidated unambiguously by extensive 2D NMR spectra [16]. On the basis of the above data, the structure of dianchinenoside C was proposed to be **1**. To our knowledge, this is the first C-23 ester linkage glycoside in a saponin [18].

Dianchinenoside D (**2**), was obtained as powder from MeOH, mp 236–238°, $[\alpha]_D^{16}-3.3°$, had a molecular formula of $C_{42}H_{66}O_{16}$ identical with **1**. Its IR and ^{13}C NMR spectral data were very similar to those of **1**, suggesting **2** to be a congener of **1**. On acid hydrolysis under the same conditions as mentioned above for **1**, **2** gave **5** and D-glucose, which were identical by TLC and GLC, respectively, with authentic samples. For clarification of the location of glucose, the ^{13}C NMR spectrum was inspected. The spectrum corresponding to the aglycone part of **2** showed signals essentially identical with those of **1**, except for the absence of a signal at *ca* δ177 indicating that one glucose residue was not attached to the aglycone via an ester bond. The sugar moiety signals at δ95.9, 75.7, 78.7, 71.0, 78.0, 73.9, 78.5, 71.6, 78.4, 62.7, matched well with those of **1**, except for G-6 at δ69.7 and G-1′ at δ105.4. The G-6 carbon signal was significantly downfield (δ62.4 in **1**; in **2** this signal appeared at δ69.7), and G-5 carbon signals were slightly shifted upfield (Table 2). These observations implied that the other glucose was bound through the glycoside linkage to the G-6 hydroxyl group of the first sugar, which was bound to the C-28 ester group of the aglycone [19]. The configurations at the anomeric position of the glucose moieties were easily assigned to be β from the coupling constants ($J=8$ Hz) of the anomeric proton signals at δ6.22 and 4.99. Therefore, **2** was 3β,16α-dihydroxyolean-12-ene 23α,28β-dioic acid 28-*O*-β-D-glucopyranosyl (1→6)-β-D-glucopyranoside.

Compound **3** displayed a HPLC peak with the longest retention time among the saponins from *D. chinensis*. Its IR spectrum afforded an absorption at 1733 cm^{-1}, indicating the presence of an ester group. Other intense absorptions were observed at 3426 cm^{-1} (hydroxyl group), 1716 cm^{-1} (carboxyl group) and 1635 cm^{-1} (double bond). A molecular formula of $C_{36}H_{56}O_{11}$ was deduced from FAB mass spectroscopy, indicating that one glucose in dianchinenoside C and D had been reduced. This reduction was also supported by the ^1H and ^{13}C NMR spectra (Tables 1 and 2). Interpretation of the COSY spectra showed H1 to H3, H15 to H16, H11 to H12, and H18 to H19 were identical with those of dianchinenosides. The remaining glucose could be placed

Table 1. ^{1}H NMR spectral data for **1**–**3** (400 MHz, pyridine-d_5)

H	1	2	3
Aglycone moiety			
3	4.66 *dd* (4, 14)	4.65 *dd* (4, 14)	4.67 *dd* (4, 13)
12	5.43 *brs*	5.62 *brs*	5.63 *brs*
15	*ca* 1.66*	*ca* 1.66*	*ca* 1.67*
	2.47 *dd* (4, 14)	2.48 *dd* (4, 14)	2.50 *dd* (4, 14)
16	5.22 *d* (4)	5.22 *brs*	5.24 *brs*
18	3.50 *dd* (4, 14)	3.52 *dd* (4, 14)	3.54 *dd* (4, 14)
19	*ca* 1.35*	*ca* 1.34*	*ca* 1.35*
	2.74 *dd* (14, 14)	2.75 *dd* (14, 14)	2.76 *dd* (14, 14)
24	1.59 *s*	1.62 *s*	1.64 *s*
25	0.99 *s*	1.05 *s*	1.04 *s*
26	0.97 *s*	0.94 *s*	0.98 *s*
27	1.69 *s*	1.78 *s*	1.79 *s*
29	1.03 *s*	1.05 *s*	1.05 *s*
30	1.16 *s*	1.15 *s*	1.16 *s*
Sugar moiety			
C-28			
Glc-1	6.29 *d* (8)	6.22 *d* (8)	6.33 *d* (8)
Glc-2	4.13 *t* (8, 8)	4.05 *dd* (8, 9)	4.15 *dd* (8, 9)
Glc-3	4.27*	4.07*	4.32 *m*
Glc-4	4.37*	4.23*	4.33 *m*
Glc-5	3.99*	4.20*	4.04 *m*
Glc-6	4.43 *dd* (2, 11)	4.33 *dd* (2, 12)	5.40 *dd* (5, 12)
	4.37*	4.30*	5.47 *dd* (2, 12)
Glc-1′		4.99 *d* (8)	
Glc-2′		3.97 *dd* (8, 9)	
Glc-3′		4.17	
Glc-4′		4.17	
Glc-5′		3.97	
Glc-6′		4.45 *dd* (4, 12)	
		4.24 *dd* (2, 12)	
C-23			
Glc-1	6.39 *d* (8)		
Glc-2	4.22 *t* (8, 8)		
Glc-3	4.27*		
Glc-4	4.31*		
Glc-5	3.99*		
Glc-6	4.43 *dd* (2, 11)		
	4.07*		
16-OH	6.27 *d* (5)	6.26 *d* (5)	6.42 *d* (5)

Coupling constants (J in Hz) are given in parentheses, the assignments were based on ^{1}H–^{1}H COSY and ^{1}H–^{13}C COSY.

Glc: β-D-glucopyranosyl.

*Obscured by other signals, therefore coupling could not be accurately determined.

on C-28 due to a pair of anomeric protons and carbons at δ6.33/95.9 by comparison with other related data of dianchinenosides [16]. Thus, **3** was secured for hainanenside isolated from *Ilex hainanensis* Merr. [17].

The other three flavonoids were identified as isoorientin-2″-*O*-glucoside (**7**), isovitexin-2″-*O*-glucoside (**8**), and chrysoeriol-7-*O*-glucoside (**9**) by comparison with their spectral data with those reported earlier [20–24]. These compounds have been isolated from *Dianthus* for the first time. Compound **10** was readily elucidated as sitosterol 3β-*O*-β-D-glucopyranoside by spectroscopic methods [25], and finally identified by direct comparison (mixed melting point determination, TLC behaviour) with an authentic sample, and **6** was found to be identical to 3-*O*-α-L-arabinopyranosyl hederagenin 28-*O*-β-D-glucopyranosyl (1→6)-β-D-glucopyranoside (**6**) by extensive 2D NMR experiments and comparison with spectroscopic data reported in the literature [26, 27], and ^{1}H and ^{13}C NMR charts provided kindly by Associate Prof. Kohda.

Table 2. ^{13}C NMR spectral data for 1–3 (100 MHz, in pyridine-d_5)

C	1*	2†	3†
Aglycone moiety			
1	39.0	39.2	39.2
2	27.6	27.3	27.9
3	75.1	75.2	75.4
4	55.3	54.8	54.5
5	52.3	52.0	52.1
6	21.3	22.1	21.8
7	33.2	33.1	33.2
8	40.5	40.6	40.5
9	47.5	47.6	47.6
10	37.0	36.7	36.9
11	23.7	23.7	23.9
12	122.7	122.6	122.6
13	144.6	144.8	144.5
14	42.0	42.6	41.9
15	36.1	36.2	36.2
16	74.4	74.3	74.4
17	49.1	49.2	49.1
18	41.3	41.3	41.3
19	47.2	47.2	47.2
20	30.8	30.8	30.5
21	36.0	36.0	36.0
22	32.2	32.1	32.3
23	177.6	181.7	180.7
24	12.0	12.3	12.3
25	16.3	16.3	16.6
26	17.5	17.6	17.5
27	27.2	27.3	27.2
28	176.0	176.1	176.0
29	33.2	33.2	33.2
30	24.7	24.7	24.6
Sugar moiety			
C-28			
Glc-1	95.9	95.9	95.9
Glc-2	74.0	75.7	74.2
Glc-3	77.9	78.7	78.9
Glc-4	71.2	71.0	71.1
Glc-5	79.4	78.0	79.4
Glc-6	62.4	69.7	62.2
Glc-1′		105.4	
Glc-2′		73.9	
Glc-3′		78.5	
Glc-4′		71 6	
Glc-5′		78.4	
Glc-6′		62.7	
C-23			
Glc-1	96.5		
Glc-2	74.5		
Glc-3	78.7		
Glc-4	71.3		
Glc-5	79.4		
Glc-6	62.3		

*Assignments were aided by ^1H–^{13}C COSY.

†Comparison with those of dianchinenoside A [16].

EXPERIMENTAL

General. Mps: uncorr. UV spectra were recorded on a Hitachi 340 spectrometer. The IR spectra were determined on a JASCO 7300 FTIR or Hitachi 260-60 spectrophotometer. Optical rotations were determined on a JASCO DIP-4 digital polarimeter. EI (70 eV energy) and FAB mass spectrometry conducted on a JEOL JMS D-300 and DX-303 mass spectrometer, respectively. ^1H and ^{13}C NMR were recorded on a JEOL GX-400 (^1H at 400 MHz, ^{13}C at 100 MHz) or a JEOL A-500 FT-NMR (^1H at 500 MHz, ^{13}C at 125 MHz) spectrometer. Standard JEOL pulse sequences were used for 2D NMR experiments. Chemical shifts are expressed in δ(ppm) downfield from TMSi as an int. standard, and coupling constants reported in Hz. TLC was carried out on silica gel 60 F_{254} and reversed-phase RP-8 (Merck), and spots were visualized under short wavelength UV light, followed by spraying with 10% H_2SO_4 and heating. Diaion HP-20 (Mitsubishi Kasei), silica gel (BW-820 MH, Fuji division and Kieselgel 60 F_{254}, Merck), polyamide (Wako C-200) and Toyopearl HF 40 were used for CC. MPLC was carried out on a silica gel column (CQ-3, 24 mm i.d. × 360 mm, Fuji gel, detector 210 nm and 254 nm for flavonoids). Prep. HPLC was performed using ODS column (Capcell pak ODS, Shiseido, 10 mm i.d. × 250 mm, detector 210 nm). GLC: 25 SE-30 on Chromsorb W (60–80 mesh), 3 mm i.d. × 1.5 m, column temp. 150°, carrier gas N_2, flow rate 40 ml min^{-1}.

Isolation of saponins. Aerial parts of the plant *D. chinensis* L. were collected by one of the authors (H.-Y. Li) from Nansan mountain, Dongliao, P. R. China in September 1989. Dried aerial parts (6 kg) of *D. chinensis* were extracted with 95% EtOH (10 l) 4 × under reflux for 1 hr. The combined EtOH extract was concd under red. pres. to an aq. suspension, which was extracted with $CHCl_3$, EtOAC, and *n*-BuOH (500 ml, 3 ×), successively. The *n*-BuOH layer was evapd *in vacuo* to give a residue (59 g), which was applied to a column of Diaion HP-20 (4.5 kg) with 30, 50, 70 and 100% MeOH to give 118 frs (400 ml, each fr.). The frs containing saponins were combined, and placed on a column of polyamide with a MeOH and H_2O system to eliminate flavonoids. The pure saponins were chromatographed over Toyopearl HW-40F with MeOH–H_2O (1:1) repetitively to obtain several saponin frs. The more polar saponin fr. was subjected to MPLC to give a powder, finally sepd by HPLC with 40% MeOH to afford dianchinenoside C (5 mg), dianchinenoside D (6 mg), 3-*O*-α-L-arabinopyranosyl hederagenin 28-*O*-β-D-glucopyranosyl (1→6)-β-D-glucopyranoside (**6**, 9 mg), and a mixt. containing hainanenside, which was further purified by HPLC with MeOH–H_2O (3:2) to yield a pure hainanenside (5 mg).

Isolation of flavonoids and sterol glycoside. The flavonoid fr. eluted from Diaion HP-20 column and the flavonoid fr. sepd from the saponin fr. were combined, and then subjected to polyamide column repetitively, followed by MPLC and ODS MPLC with $CHCl_3$–MeOH and MeOH–H_2O systems, respectively, to furnish

isoorientin-2″-*O*-glucoside (250 mg), isovitexin-2″-*O*-glucoside (25 mg) and chrysoeriol-7-*O*-glucoside (8 mg). The EtOAC extract was chromatographed over a silica gel column with $CHCl_3$–MeOH, followed by MPLC with 20% MeOH–$CHCl_3$ to give sitosterol 3β-*O*-β-D-glucopyranoside (24 mg).

Dianchinenoside C (**1**). Powder, mp 225–227°, $[\alpha]_D^{16}$ +12.4° (MeOH; *c* 0.5). IR ν_{max}^{KBr} cm^{-1}: 3402, 3377, 2926, 1734, 1709, 1651, 1595, 1558, 1456, 1386, 1223, 1072, 1033, 584, 530. FAB-MS *m/z*: 865 $[M+K]^+$, 849 $[M+Na]^+$, 687 $[M+Na-162]^+$, 503 $[M+H-glc-glc]^+$. ^1H and ^{13}C NMR data: Tables 1 and 2, respectively.

Dianchinenoside D (**2**). Powder, mp 236–238°, $[\alpha]_D^{16}$ +3.3° (MeOH; *c* 0.2). IR ν_{max}^{KBr} cm^{-1}: 3354, 2928, 2860, 1734, 1716, 1685, 1653, 1558, 1543, 1458, 1368, 1261, 1167, 1074, 1167. FAB-MS *m/z* 865 $[M+K]^+$, 849 $[M+Na]^+$, 827 $[M+H]^+$, 665 $[M+H-162]^+$, 503 $[M+H-glc-glc]^+$. ^1H and ^{13}C NMR data: Tables 1 and 2, respectively.

Acid hydrolysis of dianchinenosides C (**1**) *and D* (**2**). Dianchinenoside C (**2**, 5 mg) was dissolved in a mixt. of MeOH (2 ml) and 1M HCl (1 ml), and heated under reflux for 2 hr. After the MeOH was removed, the aq. soln was diluted with H_2O and extracted with EtOAc. The EtOAc soln was evapd to give aglycone (**5**) by direct comparison with an authentic sample. The H_2O layer was neutralized with anion-exchange resin (Amberlite MB-3), and then evapd. The residue was treated with 1-(trimethylsilyl) imidazole at 90° for 1 hr and H_2O was added to the reaction mixt. to decompose the excess reagent. The reaction product was extracted with hexane (1 ml, 3×) and the hexane layer was washed with H_2O (1 ml, 3×). The hexane soln was subjected to GLC for identification of the sugar moiety. The TMSi derivative was identified as D-glucose.

By the same method, **2** (5 mg) was hydrolysed to aglycone (**5**) and D-glucose.

Hainanenside (**3**). Powder, $[\alpha]_D^{16}$ +27.0° (MeOH; *c* 0.5). IR ν_{max}^{KBr} cm^{-1}: 3426, 2925, 2855, 2360, 1733, 1716, 1635, 1457, 1368, 1229, 1072, 418. FAB-MS *m/z*: 687 $[M+Na]^+$, 665 $[M+H]^+$, 503 $[M+H-glc]^+$. ^1H and ^{13}C NMR data: Tables 1 and 2, respectively.

3-O-α-L-*Arabinopyranosyl hederagenin* 28-O-β-D-*glucopyranosyl* (1→6)-β-D-*glucopyranoside* (**6**). Powder, $[\alpha]_D^{16}$ +15.3° (MeOH; *c* 1.1). IR ν_{max}^{KBr} cm^{-1}: 3425, 3375, 2943, 1745, 1651, 1458, 1368, 1170, 1060. FAB-MS *m/z*: 951 $[M+Na]^+$, 929 $[M+H]^+$.

Isoorientin-2″-glucoside (**7**). Yellow plates (MeOH), mp 239–241° (dec.), $[\alpha]_D^{16}$ −53.7° (pyridine; *c* 1.0). UV λ_{max}^{MeOH} nm (log ε): 268 (3.79), 344 (3.80). UV $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 278 (3.93), 300 (3.62) sh, 338 (3.45) sh, 428 (3.89). UV $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε): 280 (3.83), 344 (3.73), 412 (3.48). IR ν_{max}^{KBr} cm^{-1}: 3400, 1640, 1610, 1585, 1295, 1195, 1070. FAB-MS *m/z*: 649 $[M+Na]^+$, 611 $[M+H]^+$.

Isovitexin-2″-O-glucoside (**8**). Yellow plates (MeOH), mp 223–225° (dec.), $[\alpha]_D^{16}$ −23.0° (MeOH; *c* 0.2). UV λ_{max}^{MeOH} nm (log ε): 272 (4.32), 338 (4.32). UV $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 278 (4.40), 300 (4.26) sh, 350 (4.41), 388 (4.37). UV $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε): 272 (4.38), 340 (4.36), 402 (4.06) sh. IR ν_{max}^{KBr} cm^{-1}: 3400, 1650, 1610, 1570, 1350, 1185, 1170. FAB-MS *m/z*: 633 $[M+Na]^+$, 595 $[M+H]^+$.

Chrysoeriol-7-O-glucoside (**9**). Yellow plates (MeOH), mp 215–217° (dec.), $[\alpha]_D^{16}$ −50.5° (pyridine; *c* 0.15). UV λ_{max}^{MeOH} nm (log ε): 248 (3.85), 268 (3.73), 345 (3.85). UV $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 260 (3.73) sh, 274 (3.81), 296 (3.51) sh, 364 (3.81) sh, 390 (3.80). UV $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε): 246 (3.74), 268 (3.75), 350 (3.80), 330 (3.33) sh. IR ν_{max}^{KBr} cm^{-1}: 3400, 1840, 1650, 1600, 1490, 1340, 1300, 1250, 1200. FAB-MS *m/z*: 463 $[M+H]^+$.

Sitosterol 3β-O-β-D-*glucopyranoside* (**10**). Powder, mp 290–292°, EI-MS *m/z*: 414 $[M-glc]^+$. IR ν_{max}^{KBr} cm^{-1}: 3440, 2960, 2900, 1480, 1380, 1180, 1088, 1040.

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