Pergamon

PII: S0031-9422(96)00770-4

Phytochemistry, Vol. 45, No. 1, pp. 159–166, 1997

0031-9422/97 $17.00+0.00

LIGNAN, PHENYLPROPANOID AND IRIDOID GLYCOSIDES FROM *PEDICULARIS TORTA*

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(*Received in revised form* 11 *October* 1996)

Key Word Index—*Pedicularis torta*; Scrophulariaceae; lignan glycosides; phenylpropanoid glycosides; iridoid glucosides.

Abstract—Six new lignan glucosides, tortosides A–F were isolated from whole plants of *Pedicularis torta*, along with 11 known compounds, (+)dihydrodehydrodiconiferyl alcohol-4-*O*-α-L-rhamnopyranoside, (+)-dihydrodehydrodiconiferyl alcohol-4-*O*-β-D-glucopyranoside, (+)-dihydrodehydrodiconiferyl alcohol-9-*O*-β-D-glucopyranoside, (+)-dehydrodiconiferyl alcohol-4-*O*-β-D-glucopyranoside, cistanosides C and D, verbascoside, 8-epiloganin, gardoside methyl ester, shanzhiside methyl ester and loganic acid. On the basis of spectral and chemical evidence, tortosides A–F were determined to be epi-syringaresinol-4″-*O*-β-D-glucopyranoside, 5,5′-dimethoxylariciresinol-4′-*O*-β-D-glucopyranoside, 5′,5″-demethylsyringaresinol-4″-*O*-β-D-glucopyranoside, (+)-dehydrodiconiferyl alcohol-9-*O*-β-D-4″-*O*-methylglucopyranoside, (+)-5-methoxydihydrodehydrodiconiferyl alcohol-9′-*O*-β-D-glucopyranoside and (+)-dehydroconiferyl alcohol-8,5′-dehydroconiferyl aldehyde-9-*O*-β-D-glucopyranoside, respectively.

INTRODUCTION

In previous papers [1–6], we have reported the isolation and structural elucidation of phenylpropanoid and iridoid glycosides from the genus *Pedicularis*. In continuation of our chemical investigation, this paper describes the isolation and structural elucidation of six new lignan glucosides, tortosides A–F, and also 11 known compounds, (+)-dihydrodehydrodiconiferyl alcohol-4-*O*-α-L-rhamnoside (**7**), (+)-dihydrodehydrodiconiferyl alcohol-4-*O*-β-D-glucoside (**8**), (+)-dihydrodehydrodiconiferyl alcohol-9-*O*-β-D-glucoside (**9**), (+)-dehydrodiconiferyl alcohol-4-*O*-β-D-glucoside (**10**), cistanoside D (**11**), cistanoside C (**12**), verbascoside (**13**), 8-epiloganin, (**14**), gardoside methyl ester (**15**), shanzhiside methyl ester (**16**) and loganic acid (**17**), from whole plants of *P. torta* [7].

RESULTS AND DISCUSSION

Compounds **11**–**17** were identified on the basis of their spectral data and direct comparison (TLC) with authentic samples [**2**–**4**]. Compounds **7**–**10** were identified by comparison of their spectral data (FAB- and EI-mass spectra, ^{1}H and ^{13}C NMR, CD) with those reported in the literature [**8**–**10**].

Tortoside A (**1**) was found to have the formula $C_{28}H_{36}O_{13}$ from FAB-mass spectral, NMR and DEPT data. The ^{1}H NMR spectrum clearly indicated the presence of two pairs of equivalent aromatic protons, four aromatic methoxyl groups, one anomeric proton of glucose and a bis-tetrahydrofuran ring [11] (see Experimental), the chemical shifts of which were assigned from two-dimensional ^{1}H–^{1}H COSY. Thus, compound **1** was a 2,6-diaryl-3,7-dioxabicyclo-[3,3,0]-octane-type lignan glucoside, which was confirmed by its ^{13}C NMR spectrum (Table 1). Comparison of the ^{1}H NMR spectrum of compound **1** and the diequatorial syringaresinol-4″-*O*-β-D-monoglucoside [12], showed that the signals of H-2 and, H-6 were not identical in compound **1**, indicating that the aryl substituent of C-2 was axial, while C-6 was equatorial [13, 14]. It is estimated that the axial proton H-6 is held close to the axial aryl group at C-2 and shifted upfield, while H-2 adjacent to the axial aromatic ring is shifted downfield. In the ^{13}CNMR spectrum of compound **1**, the signal at δ 131.7 corresponded with an equatorial sinapyl group (C-1′) [15]. In the HMBC spectrum, the H-2 signal showed a cross-peak with the carbon signal at δ 133.1 (C-1″). Downfield shifts of 4.6 ppm for C-3″ and 5″, and 2.9 ppm for C-4″, relative to syringaresinol [16, 17] agreed well with a glucosyl linkage at C-4″ of the axial ring. From the

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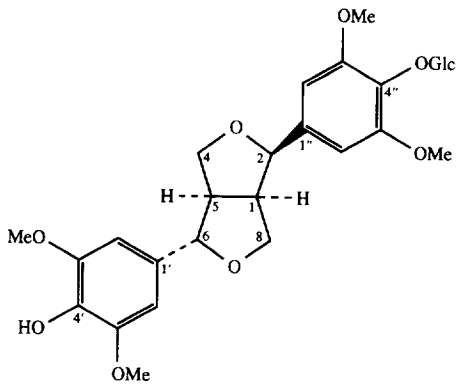

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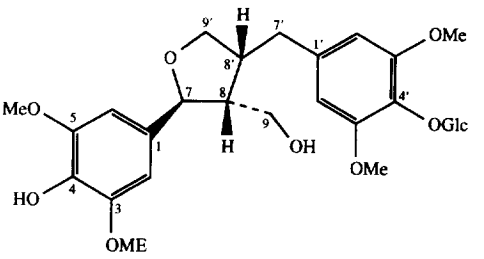

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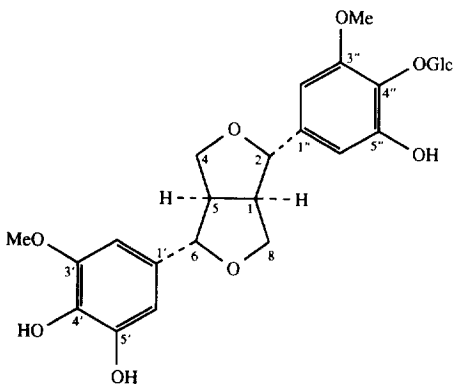

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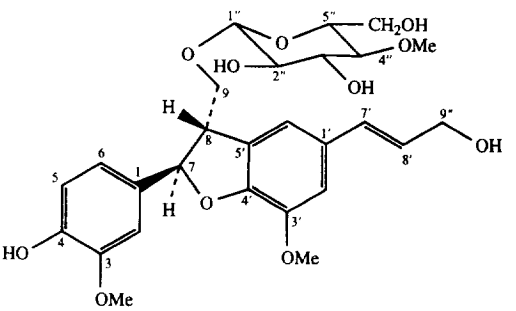

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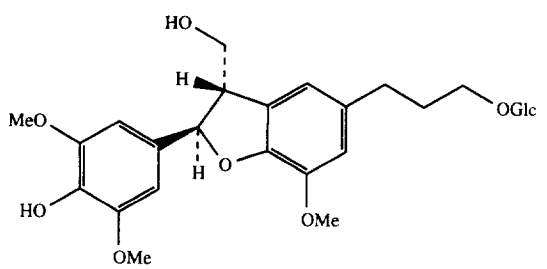

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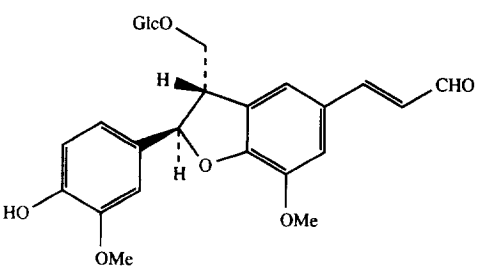

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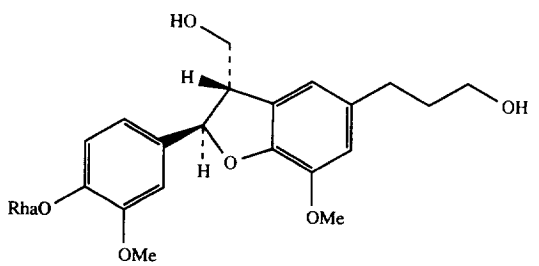

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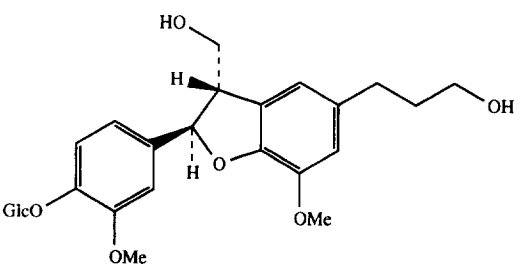

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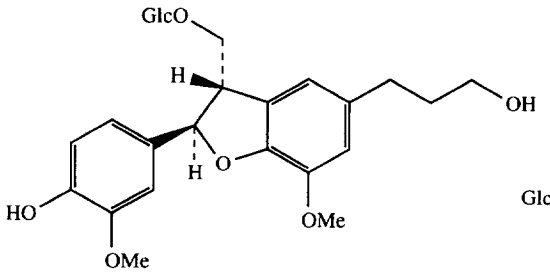

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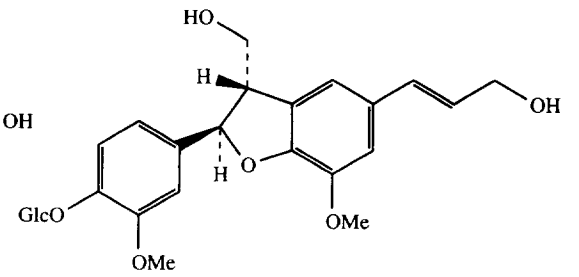

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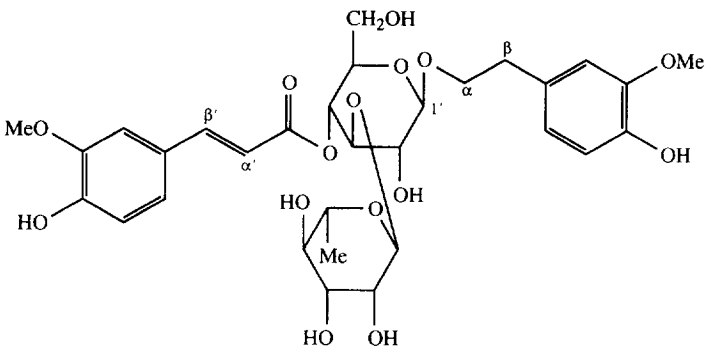

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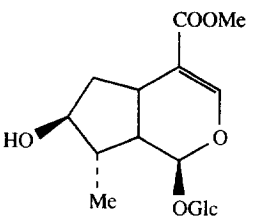

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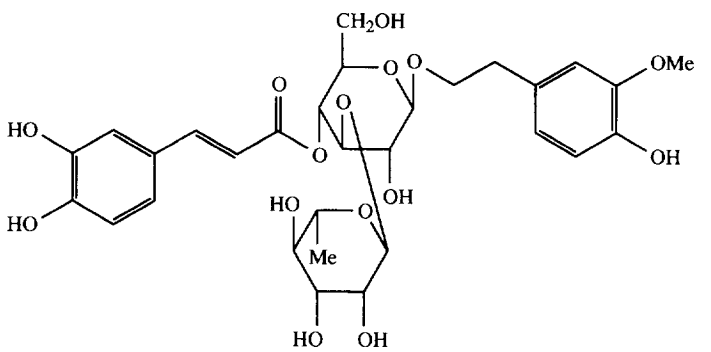

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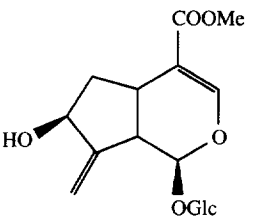

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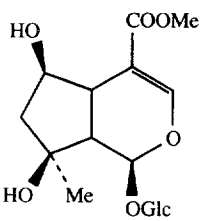

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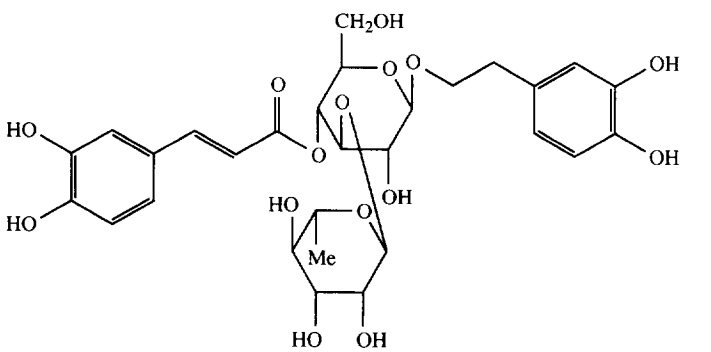

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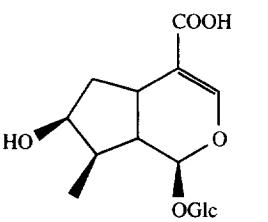

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Table 1. ^{13}C NMR data of compound **1**, syringaresinol, syringaresinol-4″-*O*-β-D-glucopyranoside and compound **3** (100 MHz, δ)

C	**1** (DMSO-d_6)	Syringaresinol (DMSO-d_6)	Syringaresiol-4″-*O*-β-D-glucopyranoside (DMSO-d_6)	**3** (CD_3OD)
1(5)	53.3 (53.1)	53.8	53.6	54.7 (54.6)
4(8)	71.4 (71.3)	71.1	71.2	75.2 (74.9)
2(6)	85.6 (85.4)	85.3	85.3 (85.1)	85.6 (85.5)
1′(1″)	131.7 (133.1)	131.5	131.4 (134.1)	135.4 (136.1)
2′(2″)	103.4 (103.4)	103.9	104.0 (104.4)	109.1 (106.5)
3′(3″)	147.7 (152.5)	147.9	148.0 (152.6)	150.6 (155.4)
4′(4″)	133.8 (137.9)	135.0	135.1 (137.2)	137.3 (136.7)
5′(5″)	147.7 (152.5)	147.9	148.0 (152.6)	141.3 (142.9)
6′(6″)	103.4 (103.4)	103.9	104.0 (104.4)	109.5 (106.6)
OMe	56.1	56.1	56.1	59.1
Glc				
1	103.1		102.9	106.0
2	73.6		74.2	76.6
3	76.1		76.5	79.2
4	69.1		70.1	72.1
5	75.6		77.1	78.6
6	60.4		61.1	63.4

above results, tortoside A (**1**) was identified as epi-syringaresinol-4″-*O*-β-D-monoglucopyranoside.

Tortoside B (**2**) had a molecular formula of $C_{28}H_{38}O_{13}$ which was suggested by its FAB-mass spectrum, NMR and DEPT data. Acid hydrolysis with 2 N HCl–MeOH yielded D-glucose. The ^1H NMR spectrum revealed the presence of four methoxyl groups, an anomeric proton for β-glucose, two singlet signals for two phenolic protons, which suggested the presence of two 3,5-dimethoxy-4-hydroxypheny moieties. The ^1H NMR spectrum also showed signals for H-7 of the tetrahydrofuran ring at δ 4.64 (1H, *d*, $J = 6.3$ Hz), which indicated that H-7 and H-8 were in a *trans*-arrangement [18 20]. Comparison between ^1H and ^{13}C NMR spectra of compound **2** and salvadoraside [21], showed that they had similar structures, except that the former was a monoglucopyranoside and the glucose was connected at C-4′, because in compound **2**, C-3, C-5, C-4 and C-1 were shifted upfield by 6.0, 6.0, 4.3 and 0.7 ppm, respectively, due to the absence of a C-4 oxygen glucose. Thus, tortoside B (**2**) was identified as 5, 5′-dimethoxylariciresinol-4′-*O*-β-D-monoglucopyranoside [22].

The FAB-mass spectrum of tortoside C (**3**) suggested the molecular formula $C_{26}H_{32}O_{13}$ which was confirmed by NMR and DEPT data. The NMR spectra showed that it was a 2,6-diaryl-3,7-dioxabicyclo-[3,3,0]-octane-type lignan glucoside. The signal at δ 4.80 (2H, *d*, $J = 6.9$ Hz) in the ^1H NMR spectrum, due to H-2 and H-6, showed that the aryl substituents at C-2 and C-6 were diequatorial [13, 14]. Except for of one the β-glucose and two methoxyl signals in the ^{13}C NMR spectrum, the other carbon signals were in pairs, the chemical shifts of which indicated the 3-methoxyl-4,5-dihydroxyl substitutions of phenyl rings. The differences in chemical resonance within these pairs [+0.7, +4.8 and +1.6 ppm (C-1″, 3″ and 5″, respectively) and −0.6, −2.6 and −2.9 ppm (C-4″, 2″ and 6″, respectively)] showed that the β-glucose was connected to the C-4″ oxygen. Thus, tortoside C (**3**) was 5′,5″-demethyl-syringaresinol-4″-*O*-β-D-monoglucopyranoside.

Tortoside D (**4**) gave a positive response to $FeCl_3$ and Molish tests, indicating that it was a glycoside with a phenolic hydroxyl group. The molecular formula, $C_{27}H_{34}O_{11}$, was deduced from the FAB-mass spectrum, NMR and DEPT data. Its ^1H NMR spectrum showed five aromatic protons, the coupling constants of which, gave the substitution pattern indicated in the formula: three methoxyl groups, an (*E*)-coniferyl alcohol side-chain and dihydrobenzofuran proton signals. The above spectral data suggested that compound **4** was a dehydrodiconiferyl alcohol-type lignan [8, 9] and its aglycone was DCG-E [23]. This was supported by significant fragements at *m/z* 137 $[ArCH_2]^+$ and 151[ArCO]$^+$ in the EI-mass spectrum. Comparison between the ^{13}C NMR spectra of **4** compound and DCG-E [23] showed that they had similar structures, except that the former had one more methoxyl group at δ 62.9 and C-4″ was shifted downfield by 15.2 ppm, while C-1″, 2″, 3″ and 5″ were shifted upfield by 4.5, 1.8, 1.0 and 1.2 ppm, respectively, which indicated that **4** was a 4″-*O*-methoxyl-glucopyranoside [24]. This was confirmed by the fragment peaks at *m/z* 358 $[M-176]^+$ and 340 $[M-176-H_2O]^+$ in the FAB-mass spectrum. In ^1H NMR spectrum the anomeric proton signal at δ 4.89 (1H, *d*, $J = 7.5$ Hz, H-1″) led to the assignment of 4″-*O*-methyl glucose to the β-configuration. The difference between compound **4** and dehydrodiconiferyl alcohol [25] in their ^{13}C NMR spectra showed that the glucosyl linkage was at the C-9 oxygen (C-9 was shifted downfield δ 69.6). The stereochemistry of the dihydrofuran ring was determined by NOE and CD experiments. A

positive NOE between H-7 and H-9 indicated the *cis*-arrangements. The CD curve of compound **4** exhibited a positive Cotton effect at 284 nm, providing evidence that the configuration in compound **4** must be 7*R*, 8*S* [10, 23]. According to above data, tortoside D (**4**) was established as (7*R*, 8*S*)-dehydrodiconiferyl alcohol-9-*O*-*β*-D-4″-*O*-methylglucopyranoside.

Tortoside E (**5**) also gave positive reactions to $FeCl_3$ and Molish reactions. The FAB-mass spectrum indicated the molecular formula $C_{27}H_{36}O_{12}$, which was confirmed by the NMR, and DEPT data. The ^1H NMR spectrum of **5** showed the presence of four aromatic protons, three methoxyl groups, protons of a dihydroconiferyl alcohol side-chain and a dihydrobenzofuran ring. The strong peaks at *m/z* 167 and 181 in the EI-mass spectrum showed the presence of a 3,5-dimethoxyl-4-hydroxylphenyl group. The differences between compound **5** and DCG-G [23] in their ^{13}C NMR spectra was in the presence of two methylene groups in **5**, instead of the *trans* double-bond in DCG-G. These results indicated that compound **5** was a 5-methoxyl-dihydrodedydrodiconiferyl alcohol-glucopyranoside [9]. In dihydrodehydrodiconiferyl alcohol, the signals for C-7′, -8′ and -9′ are at δ 32.7, 36.0 and 63.0, respectively [8, 9], whereas compound in **5** the signals for C-9′ and C-8′ were at δ 71.8 (+8.8 ppm) and δ 28.9 (−7.1 ppm), respectively, which showed that the glucosyl linkage was at the C-9′ oxygen. The NOE spectrum showed that H-7 and H-8 had *trans*-arrangements. The CD curve of compound **5** confirmed that it had the 7*R*,8*S*-configuration [10, 23]. From the above results, the structure of tortoside E (**5**) was elucidated as (7*R*,8*S*)-5-methoxyl-dihydrodehydrodiconiferyl alcohol-9′-*O*-*β*-D-glucopyranoside.

Tortoside F (**6**) had the molecular formula, $C_{26}H_{30}O_{11}$. Its ^1H NMR spectrum indicated the presence of five aromatic protons, two methoxyl groups, an anomeric proton of a sugar, an *α*,*β*-unsaturated aldehyde side-chain and a dihydrobenzofuran ring. These data showed that compound **6** was a dihydrobenzofuran-type lignan glycoside [8, 9], whose structure was similar to plucheoside D [26], except that the signal for shifted H-7 was shifted upfield by 0.4 ppm. In the ^{13}C NMR spectrum, the signal for C-9 was shifted to 70.1 ppm, revealing that the glucosyl linkage was at the C-9 oxygen. NOE experiments showed that H-7 and H-9 were in a *cis* arrangement, while H-7 and H-8 were in *trans* arrangement. The CD spectrum confirmed a 7*R*,8*S*-configuration [10, 23]. Thus, tortoside F (**6**) was determined as (7*R*,8*S*)-dehydrodiconiferyl alcohol-8,5′-dehydroconiferyl aldehyde-9-*O*-*β*-D-glucopyranoside.

EXPERIMENTAL

General. ^1H and ^{13}C NMR were recorded at 400 and 100 MHz, respectively, in FT mode.

Plant material. Pedicularis torta Maxim was collected in Zhang County, Gansu Province, in August, 1988. It was identified by Prof. Zhang Guo-liang of Lanzhou University and a voucher specimen (933103) is deposited in the herbarium of the authors' Institute.

Extraction and purification. Dried whole plants (5 kg) were extracted with 95% EtOH (3 × 5 l). After concn of the combined extracts almost to dryness under red. pres., hot H_2O was added and the water-insol. material removed by filtration through Celite. The filtrate was extracted successively with petrol (60–90) and *n*-BuOH. The *n*-BuOH extract was evapd to obtain a crude syrup, which was chromatographed over a polyamide column eluting with H_2O to obtain part I and then with MeOH–H_2O (1 : 1) to obtain part II.

Part I was chromatographed repeatedly by silica gel CC eluting with $CHCl_3$–MeOH (4 : 1) to obtain the pure iridoid glucosides 14 (20 mg), **15** (15 mg), **16** (50 mg) and **17** (100 mg). Part II was also chromatographed by silica gel CC eluting with $CHCl_3$–MeOH (12 : 1), followed by increasing concns of MeOH; 6 frs were collected. Fr. 1 was chromatographed by silica gel CC, eluting with $CHCl_3$–MeOH (12 : 1) to give pure compound **1** (80 mg). Fr. 2 was also subjected to silica gel CC, eluting with EtOAc–95% EtOH (10 : 1) to give **11** (45 mg). Fr.3 after silica gel CC, eluted with EtOAc–95% EtOH (8 : 1) yielding pure **2** (15 mg) and **3** (30 mg). Fr.4 after silica gel CC eluted with EtOAc–*n*-BuOH–H_2O (20 : 8 : 1) give pure **4** (65 mg), **5** (60 mg) and **6** (15 mg). Fr. 5 was purified by HPLC on a ODS-C_{18} column eluting with 40% MeOH–H_2O to obtain pure **7** (10 mg), **8** (28 mg), **9** (20 mg) and **10** (25 mg). Fr. 6 was subjected to silica gel CC eluting with EtOAc–95% EtOH (3 : 1) to obtain pure **12** (20 mg) and **13** (150 mg).

Tortoside A (**1**). Amorphous powder. $[\alpha]_D^{15}$ +28.3 (MeOH, *c* 0.32). IR ν_{max}^{KBr} (cm^{-1}): 3412, 2934, 2870, 1596, 1518, 1463, 1422, 1376, 1328, 1223, 1122, 1064, 1009, 897, 824, 750, 703. ^1H NMR (D_2O, DSS): δ 3.08 (1H, *m*, H-5), 3.34 (2H, *m*, H-1, 8a), 3.60–3.95 (*m*, H-8e, 4a), 3.80, 3.86 (each 6H, *s*, 4 × OMe), 4.15 (1H, *dd*, *J* = 8.8, 10.4 Hz, H-4e), 4.20 (1H, *d*, *J* = 6.8Hz, H-6a), 4.74 (1H, *d*, *J* = 4.2Hz, H-2e), 5.02 (1H, *d*, *J* = 7.2Hz, Glc, H-1), 6.62 (2H, *d*, *J* = 1.2 Hz, H-2′, 6′), 6.71 (2H, *d*, *J* = 1.2 Hz, H-2″, 6″) (assignment from 2D ^1H–^1H COSY experiment). ^{13}C NMR: Table 1. FAB-MS (S-Gly) *m/z*: 587 $[M + Li]^+$, 603 $[M + Na]^+$. EI-MS *m/z*: 418 $[M - 162]^+$, 236, 235, 193, 182, 181, 167, 153.

Tortoside B (**2**). Amorphous powder. $[\alpha]_D^{15}$ −85 (MeOH, *c* 0.12). IR ν_{max}^{KBr} (cm^{-1}): 3419, 3005, 2936, 2867, 2839, 1594, 1516, 1462, 1425, 1374, 1332, 1226, 1122, 1053, 898, 823, 751, 703. ^1H NMR (DMSO-d_6, TMS): δ 2.62 (1H, *m*, H-8), 2.85 (1H, *dd*, *J* = 13.5, 3.9 Hz, H-7′a), 3.16 (1H, *dd*, *J* = 13.5, 10.8 Hz, H-7′b), 2.99 (1H, *m*, H-8′), 3.58 (1H, *dd*, *J* = 6.5, 8.4 Hz, H-9′a), 3.66 (2H, *dd*, *J* = 11.4, 8.4 Hz, H_2-9), 3.71, 3.72 (each 6H, *s*, 4 × OMe), 3.90 (1H, *dd*, *J* = 6.5, 8.0 Hz, H-9′b), 4.64 (1H, *d*, *J* = 6.3 Hz, H-7), 4.83 (1H, *d*, *J* = 7.3 Hz, Glc, H-1), 6.50 (2H, *d*, *J* = 1.2 Hz, H-2′, 6′), 6.53 (2H, *d*, *J* = 1.2 Hz, H-2, 6). ^{13}C NMR: Table

Table 2. ^{13}C NMR data of compound **2** and salvadoraside

C	**2** (DMSO-d_6)	Salvadoraside (pyridine-d_5)
1	133.7	134.3
2.6	103.3	104.5
3.5	147.7	153.7
4	136.6	140.9
7	81.9	83.2
8	52.3	53.5
9	58.6	60.1
1′	132.8	135.5
2′,6′	106.8	107.3
3′,5′	152.4	153.7
4′	134.5	137.0
7′	32.8	34.0
8′	41.6	42.9
9′	71.8	73.0
OMe	56.3, 56.0	56.5
Glc		
1	102.8	105.1, 105.1
2	74.1	76.0, 76.0
3	76.4	78.3, 78.3
4	69.9	71.5, 71.5
5	77.0	78.6, 78.5
6	60.9	62.5, 62.5

2. FAB-MS (S-Gly) *m/z*: 589 $[M + Li]^+$, 605 $[M + Na]^+$.

Tortoside C (**3**). Amorphous powder. $[\alpha]_D^{15}$ −8.9 (MeOH, *c* 0.36). IR ν_{max}^{KBr} (cm^{-1}): 3411, 2936, 2881, 1596, 1519, 1463, 1430, 1332, 1223, 1122, 1072, 829, 752. ^{1}H NMR (DMSO-d_6, TMS): δ 2.72–2.94 (2H, *m*, H-1, 5), 3.40–3.80 (H of sugar), 3.83 (6H, *s*, 2 × OMe), 4.05 (2H, *dd*, *J* = 6.7, 8.0 Hz, H-4e, 8e), 4.20, 4.26 (each 1H, *d*, *J* = 6.0, 5.1 Hz, resp. H-8a, 4a), 4.80 (2H, *d*, *J* = 6.9 Hz, H-2, 6), 4.98 (1H, *d*, *J* = 7.6 Hz, Glc, H-1), 6.59, 6.67, 6.70, 6.73 (each 1H, *d*, *J* = 1.5 Hz, H-2′, 6′, 2″, 6″). ^{13}CNMR: Table 1. FAB-MS (S-Gly) *m/z*: 559 $[M + Li]^+$, 575 $[M + Na]^+$.

Tortoside D (**4**). Amorphous powder. $[\alpha]_D^{14}$ +25.2 (MeOH, *c* 1.31). ^{1}H NMR (DMSO-d_6, TMS): δ 3.39 (3H, *s*, 4″-OMe), 3.73 (1H, *m*, H-8), 3.75 (3H, *s*, 3-OMe), 3.81 (3H, *s*, 3′-OMe), 4.18 (2H, *dd*, *J* = 12.0, 6.7 Hz, H-9), 4.58 (2H, *dd*, *J* = 5.0, 1.5 Hz, H-9′), 4.89 (1H, *d*, *J* = 7.5 Hz, Glc H-1″), 5.53 (1H, *d*, *J* = 6.2 Hz, H-7), 6.23 (1H, *dt*, *J* = 16.0, 5.0 Hz, H-8′), 6.45 (1H, *d*, *J* = 16.0 Hz, H-7′), 6.86 (1H, *d*, *J* = 8.4 Hz, H-5), 6.93 (2H, *d*, *J* = 1.2 Hz, H-2′, 6′), 6.97 (1H, *d*, *J* = 1.2 Hz, H-2), 7.31 (1H, *dd*, *J* = 8.4, 1.2 Hz, H-6). ^{13}C NMR: Table 3; FAB-MS (S-Gly) *m/z*: 541 $[M + Li]^+$, 557 $[M + Na]^+$. EI-MS *m/z*: 358, 340, 298, 151, 137, 115, 91, 73, 60. CD (MeOH): $[\theta]_{284}$ = +518 , $\Delta\varepsilon_{284}$ = +0.18 (l mol^{-1} cm^{-1}).

Tortoside E (**5**). Amorphous powder. $[\alpha]_D^{14}$ +3.3 (MeOH, *c* 6.1). IR ν_{max}^{KBr} (cm^{-1}): 3410, 2928, 2871, 1598, 1515, 1462, 1422, 1370, 1334, 1236, 1124, 1069, 1035, 608. ^{1}H NMR (DMSO-d_6, TMS): δ 2.23 (2H, *m*, H-8′), 3.10 (2H, *m*, H-7′), 3.74 (6H, *s*, 3, 5-OMe), 3.77 (3H, *s*, 3′-OMe), 3.90 (1H, *m*, H-8), 4.15 (2H, *dd*, *J* = 12.0, 6.5 Hz, H-9), 4.32 (2H, *t*, *J* = 6.0 Hz, H-9′), 4.37 (1H, *d*, *J* = 7.9Hz, Glc. H-1″), 4.93 (1H, *d*, *J* = 6.5Hz, H-7), 6.58 (2H, *s*, H-2, 6), 6.66 (1H, *d*, *J* = 1.5 Hz, H-6′), 6.73 (1H, *d*, *J* = 1.5 Hz, H-2′). ^{13}CNMR: Table 3. FAB-MS (S-Gly) *m/z*: 559 $[M + Li]^+$, 575 $[M + Na]^+$. EI-MS *m/z*: 390 $[M - 162]^+$, 372, 341, 314, 271, 210, 183, 181, 167, 137, 73, 60. CD (MeOH): $[\theta]_{288}$ = +181 , $\Delta\varepsilon_{288}$ = +0.1 (l mol^{-1} cm^{-1}).

Tortoside F (**6**). Amorphous powder. $[\alpha]_D^{14}$ +35.9 (MeOH, *c* 0.32). ^{1}H NMR (DMSO-d_6, TMS): δ 3.65 (1H, *m*, H-8), 3.76 (3H, *s*, 3-OMe), 3.83 (3H, *s*, 3′-OMe), 3.70, 4.04 (each 1H, *dd*, *J* = 6.5, 12.0 Hz, H$_2$-9), 4.26 (1H, *d*, *J* = 7.9 Hz, Glc, H-1), 5.60 (1H, *d*, *J* = 6.1 Hz, H-7), 6.76 (1H, *dd*, *J* = 15.7, 7.8 Hz, H-8′), 6.79 (1H, *d*, *J* = 8.0 Hz, H-5), 6.94 (2H, *s*, H-2′, 6′), 7.32 (1H, *d*, *J* = 1.8 Hz, H-2), 7.39 (1H, *dd*, *J* = 8.0, 1.8Hz, H-6), 7.64 (1H, *d*, *J* = 15.7Hz, H-7′), 9.12 (1H, *s*, Ar-OH), 9.59 (1H, *d*, *J* = 7.8 Hz, H-9′). ^{13}CNMR: Table 3. FAB-MS (S-Gly) *m/z*: 525 $[M + Li]^+$, 541 $[M + Na]^+$. CD (MeOH): $[\theta]_{284}$ = +7700 , $\Delta\varepsilon_{284}$ = +2.33 (l mol^{-1} cm^{-1}).

(+)-*Dihydrodehydrodiconiferyl alcohol*-4-O-α-L-*rhamnopyranoside* (**7**). Amorphous powder. $[\alpha]_D^{15}$ +28.0 (MeOH, *c* 1.32). UV λ_{max}^{MeOH} (nm): 255, 280. ^{1}H NMR (pyridine-d_5, TMS): δ 1.59 (3H, *d*, *J* = 6.0 Hz, Rha H-6″), 2.08 (2H, *m*, H-8′), 2.87 (2H, *dd*, *J* = 8.0, 7.0 Hz, H-7′), 3.86 (6H, *s*, 2 × OMe), 3.93 (2H, *t*, *J* = 7.0 Hz, H-9), 6.07 (1H, *br* s, Rha H-1″), 6.10 (1H, *d*, *J* = 6.0 Hz, H-7), 6.95, 7.04 (each 1H, *d*, *J* = 1.2 Hz, H-2′, 6′), 7.20–7.60 (3H, *m*, H-2, 5, 6). ^{13}C NMR: Table 3. FAB-MS (S-Gly) *m/z*: 513 $[M + Li]^+$, 529 $[M + Na]^+$. CD (MeOH): $[\theta]_{279}$ = +4700 , $\Delta\varepsilon_{279}$ = +1.42 (mol^{-1} cm^{-1}). Spectral data identical to ref. [8].

(+)-*Dihydrodehydrodiconiferyl alcohol*-4-O-β-D-*glucopyranoside* (**8**). Amorphous powder. $[\alpha]_D^{15}$ +33.6 (MeOH, *c* 0.4). ^{1}H NMR (pyridine-d_5, TMS): δ 2.09 (2H, *m*, H-8′), 2.87 (2H, *t*, *J* = 8.0, 7.0 Hz, H-7′), 3.85, 3.62 (each 3H, *s*, 2 × OMe), 3.89 (1H, *m*, H-8), 3.93 (2H, *t*, *J* = 6.0 Hz, H-9), 5.56 (1H, *d*, *J* = 7.0 Hz, Glc, H-1″), 6.05 (1H, *d*, *J* = 6.0 Hz, H-7), 6.92, 7.05 (each 1H, *d*, *J* = 2.0 Hz, H-2′, 6′), 7.19 (1H, *dd*, *J* = 8.0, 2.0 Hz, H-6), 7.33 (1H, *d*, *J* = 2.0Hz, H-2), 7.52 (1H, *d*, *J* = 8.0Hz, H-5). ^{13}C NMR: Table 3. FAB-MS (S-Gly) *m/z*: 529 $[M + Li]^+$, 545 $[M + Na]^+$. CD (MeOH): $[\theta]_{287}$ = +6270 , $\Delta\varepsilon_{287}$ = +1.90 (l mol^{-1} cm^{-1}). Spectral data identical to refs [8, 9].

(+)-*Dihydrodehydrodiconiferyl alcohol*-9-O-β-D-*glucopyranoside* (**9**). Amorphous powder. $[\alpha]_D^{15}$ +35.6 (MeOH, *c* 0.20). UV λ_{max}^{MeOH} (nm): 279, 227, 203. ^{1}H NMR (CD$_3$OD, TMS): δ 2.88 (2H, *t*, *J* = 8.0 Hz, H-7′), 3.83, 3.66 (each 3H, *s*, 2 × OMe), 3.92 (2H, *t*, *J* = 6.0 Hz, H-9), 4.97 (1H, *d*, *J* = 7.0 Hz, Glc, H-1″), 5.97 (1H, *d*, *J* = 6.0 Hz, H-7), 6.92, 7.09 (each 1H, *d*, *J* = 1.0 Hz, H-2′, 6′), 7.14 (1H, *d*, *J* = 8.0, H-5), 7.25 (1H, *dd*, *J* = 8.0, 2.0Hz, H-6), 7.37 (1H, *d*, *J* = 2.0 Hz, H-2). ^{13}C NMR: Table 3. FAB-MS (S-Gly) *m/z*: 529 $[M + Li]^+$, 545 $[M + Na]^+$. CD (MeOH): $[\theta]_{287}$ = +2080 , $\Delta\varepsilon_{286}$ = +0.63 (l mol^{-1} cm^{-1}). Spectral data identical to ref. [9].

Table 3. ^{13}C NMR data of compounds **4**–**10** (100MHz, δ)

C	**4**(DMSO-d_6)	**5**(DMSO-d_6)	**6**(DMSO-d_6)	**7**(DMSO-d_6)	**8**(DMSO-d_6)	**9**(CD_3OD)	**10**(CD_3OD)
Aglycone							
1(1′)	135.3 (130.6)	131.6 (128.4)	131.6 (127.9)	137.0 (132.3)	136.3 (132.2)	133.8 (130.1)	138.1 (129.9)
2(2′)	110.5 (110.5)	105.4 (112.7)	110.5 (112.8)	111.5 (111.5)	110.6 (110.6)	111.4 (113.4)	111.3 (112.2)
3(3′)	149.0 (143.6)	147.5 (144.6)	146.1 (144.2)	146.0 (144.7)	147.8 (145.5)	148.0 (142.3)	150.4 (145.6)
4(4′)	146.2 (147.0)	139.6 (152.4)	147.0 (150.7)	152.6 (147.8)	152.7 (148.5)	149.2 (147.5)	149.3 (148.5)
5(5′)	114.9 (129.2)	147.5 (130.1)	115.4 (129.6)	119.2 (136.4)	118.6 (136.3)	116.2 (136.5)	116.6 (132.8)
6(6′)	117.7 (115.5)	105.4 (120.6)	119.5 (118.6)	119.2 (119.2)	118.6 (119.2)	122.1 (119.6)	119.4 (118.1)
7(7′)	86.8 (128.9)	81.8 (32.0)	87.9 (154.2)	86.3 (34.6)	85.1 (34.6)	83.8 (33.6)	88.9 (131.9)
8(8′)	53.2 (128.0)	52.2 (28.9)	50.1 (126.3)	53.5 (36.4)	53.5 (36.4)	54.1 (36.4)	53.2 (127.7)
9(9′)	69.6 (61.6)	60.9 (71.8)	70.1 (194.3)	61.3 (59.8)	61.3 (60.4)	73.7 (60.5)	65.0 (63.9)
OMe	55.7, 55.8	56.4, 55.6	55.9, 55.7	56.0, 55.7	56.0, 55.7	56.7, 56.4	56.7, 55.4
Sugar							
1″	100.2	103.6	102.9	100.4	103.4	102.9	102.8
2″	73.1	74.1	73.6	71.9	73.3	74.9	74.9
3″	76.9	77.1	77.0	71.0	76.9	78.2	78.2
4″	86.8	69.9	70.0	73.3	71.3	71.4	71.4
5″	76.7	76.5	76.8	69.8	76.8	77.9	77.9
6″	60.6	61.4	61.1	18.4	60.7	62.5	62.5
4″-OMe	62.9						

(+)-*Dehydrodiconiferyl alcohol*-4-O-β-D-*glucopyranoside* (**10**). Amorphous powder. UV $\lambda_{max}^{H_2O}$ (nm): 310, 276, 221, 203. ^1H NMR (H_2O, DSS. δ 3.87 (3H, *s*, 3-OMe), 3.94 (3H, *s*, 3′-OMe), 4.28 (2H, *dd*, J = 5.1, 5.6 Hz, H-9′), 5.12 (1H, *d*, J = 7.8 Hz, Glc, H-1″), 5.68 (1H, *d*, J = 5.6 Hz, H-7), 6.28 (1H, *dt*, J = 15.5, 5.1 Hz, H-8′), 6.57 (1H, *d*, J = 15.5 Hz, H-7′), 7.01 (1H, *d*, J = 8.0 Hz, H-5), 7.11, 7.06 (1H, *s*, H-2′, 6′), 7.10 (1H, *d*, J = 2.0Hz, H-2), 7.19 (1H, *dd*, J = 8.0, 2.0 Hz, H-6). ^{13}C NMR: Table 3. FAB-MS (S-Gly) *m/z*: 527 $[M + Li]^+$, 543 $[M + Na]^+$. CD (H_2O): $\Delta\varepsilon_{270} = +4.3$, $\Delta\varepsilon_{285} = +5.7$ (mol^{-1} cm^{-1}). Spectral data identical to ref. [10].

Cistanoside D (**11**). Amorphous powder. Spectral data as ref. [27].

Cistanoside C (**12**). Amorphous powder. Spectral data as ref. [27].

Verbascoside (**13**). Amorphous powder. Spectral data as ref. [1].

8-*Epiloganin* (**14**). Amorphous powder. Spectral data as ref. [3].

Gardoside methyl ester (**15**). Amorphous powder. Spectral data as ref. [2].

Shanzhiside methyl ester (**16**). Amorphous powder. Spectral data as ref. [2].

Loganic acid (**17**). Amorphous powder. Spectral data as ref. [28].

Acknowledgement—This work was supported by the National Natural Science Foundation of China.

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