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ISOPRENOID-SUBSTITUTED FLAVONOIDS FROM ROOTS OF *GLYCYRRHIZA INFLATA**

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Key Word Index—*Glycyrrhiza inflata*; Leguminosae; roots; licorice; kanzoh; prenylated dibenzoylmethane; pyranochalcone; 2-arylbenzofuran; isoflavan; glyinflanins E–K.

Abstract—Two new isoprenoid-substituted dibenzoylmethanes, glyinflanins E and F, a pyranochalcone, glyinflanin G, a 2-arylbenzofuran, glyinflanin H, a 6-prenylated pyranoisoflavan, glyinflanin I, and two dipyranoisoflavans, glyinflanins J and K, along with four known flavonoids were isolated from the roots of *Glycyrrhiza inflata*. Their structures were elucidated by spectroscopic methods.

INTRODUCTION

In previous papers, we reported new isoprenoid-substituted flavonoids from the aerial parts and/or roots of Chinese licorice (kanzoh in Japanese), *Glycyrrhiza uralensis*, *G. pallidiflora*, *G. eurycarpa*, *G. aspera* and *G. glabra* [1–4]. We also reported four new isoprenoid-substituted dibenzoylmethanes, glyinflanins A–D, along with nine known flavonoids from the roots of *G. inflata* collected in Jinta County, Gansu Province of China [5, 6].‡ In continuation of our study on Chinese licorice, we report herein the isolation of two new isoprenoid-substituted dibenzoylmethanes, glyinflanins E (**1**) and F (**2**), a pyranochalcone, glyinflanin G (**3**), a 2-arylbenzofuran, glyinflanin H (**4**), a 6-prenylated pyranoisoflavan, glyinflanin I (**5**), and two dipyranoisoflavans, glyinflanins J (**6**) and K (**7**), along with known compounds, isoderrone [7], licoisoflavone B [8], 8-[γ,γ-dimethylallyl)-wighteone [9], gancaonin Z [(*R*)-7,2′-hydroxy-4′-methoxy-3′-prenylisoflavan] [10] and phaseollin [11].

RESULTS AND DISCUSSION

Glyinflanin E (**1**), $C_{25}H_{28}O_6$, gave a yellowish green colour with the methanolic ferric chloride test on a TLC plate. The UV spectrum of **1** resembled those of dibenzoylmethane derivatives, such as glyinflanin A (**8**) [5]. The ^{1}H NMR spectrum (acetone-d_6) appeared as the equilibrium mixture of a dibenzoylmethane (**1**) and a β-hydroxychalcone moiety (**1′**, a tautomer of dibenzoylmethane) in solution (the ratio of **1** to **1′** was *ca* 3:7, Table 1). The ^{1}H NMR spectrum showed singlet signals at δ4.58 (0.6H, H-2 of the dibenzoylmethane form), 6.93 (0.7H, H-2 of the β-hydroxychalcone form), 12.36 (0.3H, OH-2′ of the dibenzoylmethane form), 12.25 and 15.76 (each 0.7 H, OH-2′ and OH-3 of the β-hydroxychalcone form, respectively); these signals disappeared on addition of methanol-d_4. The disappearance of the H-2 signals is attributed to the protons of the dibenzoylmethane existing in an equilibrium mixture of the keto and enol forms in the solution [5]. All other signals, i.e. the signals of a prenyl group, a 2-hydroxy-3-methyl-3-butenyl group, two singlet aromatic protons (A ring) and ABX-type aromatic protons (B ring), appeared as pairs arising from the two tautomeric structures. The spectrum resembled that of **8**, except for the 2-hydroxy-3-methyl-3-butenyl group (Table 1). The mass spectrum showed a characteristic fragment ion at *m/z* 205 ($C_{12}H_{13}O_3$, **1a** and **1b**). The presence of the prenyl group at the C-5′ position was confirmed by NOE measurement; when the methylene signal of the prenyl group at δ3.26 was irradiated, an enhancement was observed at one of the singlet signals of the aromatic protons (δ7.77 for H-6′ of the enol form). From the above data, the structures of the keto and enol forms of glyinflanin E are deduced as **1** and **1′**, respectively, except for the stereochemistry at the C-8″ position.

Glyinflanin F (**2**), $C_{25}H_{28}O_6$, gave a yellowishgreen colour with the methanolic ferric chloride test on a TLC plate. The UV spectrum resembled those of dibenzoylmethane derivatives, such as **1** and **8**. The ^{1}H and ^{13}C NMR spectra also indicated that the compound was a dibenzoylmethane derivative as follows. The spectra showed characteristic signals at the C-2 position of the keto form [δ_H 4.60 (0.8 H, *s*), δ_C 49.9] and the enol form [δ_H 6.96 (0.6 H, *s*), δ_C 91.1] [5]. The ^{1}H NMR spectrum showed the signals of hydrogen-bonded hydroxyl groups at δ12.83 (0.4 H, *s*, OH-2′ of dibenzoylmethane form), δ12.69 (0.6H, *br s*, OH-2′ of β-hydroxychalcone form) and

*Part 18 in the series 'Phenolic constituents of *Glycyrrhiza* species'. For Part 17, see ref. [10].

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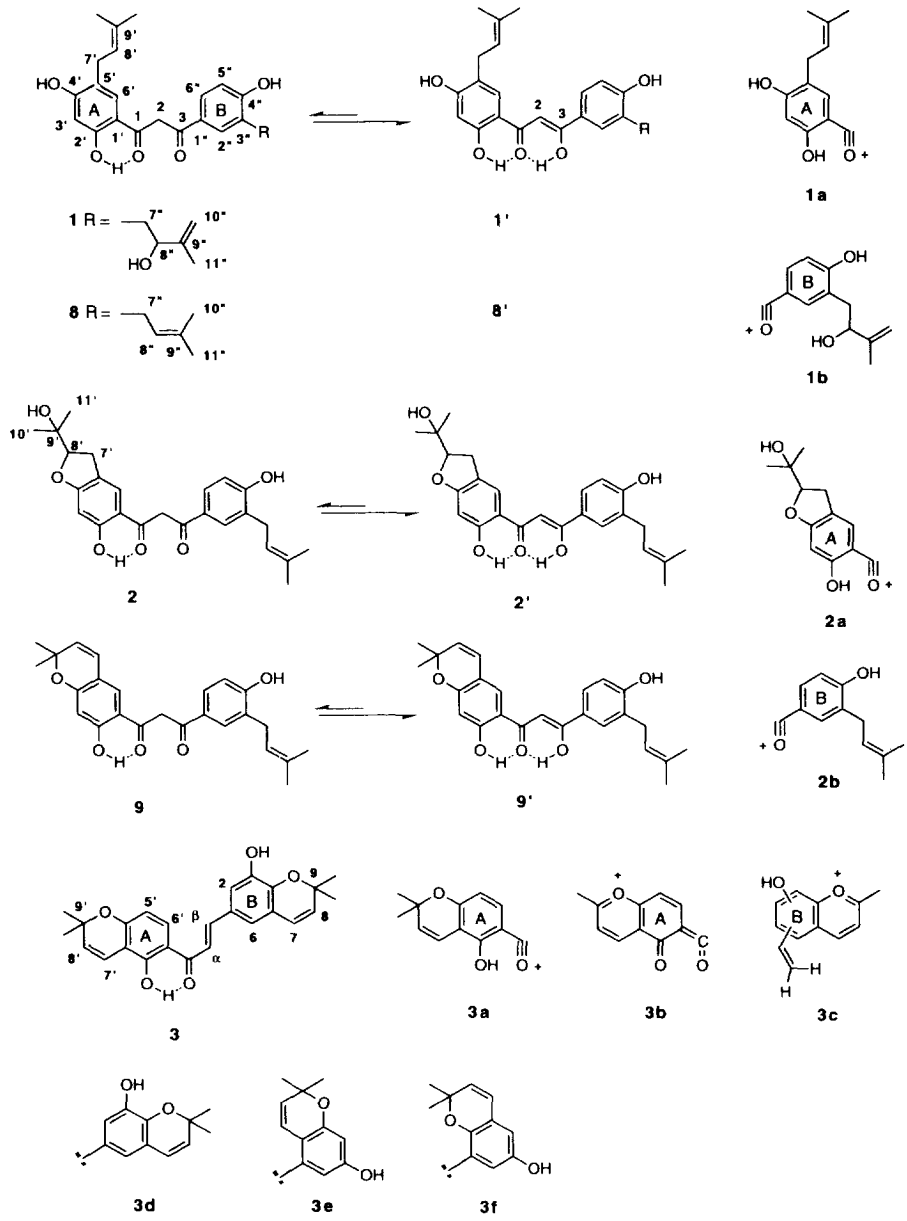
‡The known compounds are licochalcone A, glabrone, euchrestaflavanone A, euchrenone a_5, 6,3′-diprenylnaringenin, angustone B, prenyllicoflavone A, echinatin and isoliquiritigenin [6].

Table 1. ^{1}H NMR spectral data of compounds **1**, **2**, **8** and **9** (in acetone-d_6, 500 MHz)

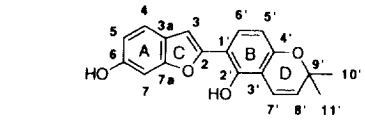
H	1′ (enol form)	1 (keto form)	8′ (enol form)	8 (keto form)	2′ (enol form)	2 (keto form)	9′ (enol form)	9 (keto form)
2	6.93 0.7H, *s*	4.58 0.6H, *s*	6.90 0.6H, *s*	4.56 0.8H, *s*	6.96 0.6H, *s*	4.60 0.8H, *s*	6.98 0.7H, *s*	4.62 0.6H, *s*
3′	6.38 0.7H, *s*	6.35 0.3H, *s*	6.38 0.6H, *s*	6.36 0.4H, *s*	6.22 0.6H, *s*	6.21 0.4H, *s*	6.24 0.7H, *s*	6.23 0.3H, *s*
6′	7.77 0.7H, *s*	7.59 0.3H, *s*	7.75 0.6H, *s*	7.58 0.4H, *s*	7.87 0.6H, *br t* (1)	7.72 0.4H, *br t*	7.84 0.7H, *s*	7.67 0.3H, *s*
2″	7.84 0.7H, *d* (2)	7.87 0.3H, *d*	7.80 0.6H, *d*	7.82 0.4H, *d*	7.85 0.6H, *d* (2)	7.82 0.4H, *d*	7.84 0.7H, *d*	7.81 0.3H, *d*
5″	6.94 0.7H, *d* (8)	6.92 0.3H, *d*	6.97 0.6H, *d*	6.95 0.4H, *dd*	6.96 0.6H, *d* (8)	6.94 0.4H, *d*	6.96 0.7H, *d*	6.94 0.3H, *d*
6″	7.80 0.7H, *dd* (2, 8)	7.83 0.3H, *dd*	7.75 0.6H, *dd*	7.79 0.4H, *dd*	7.81 0.6H, *dd* (2, 8)	7.78 0.4H, *dd*	7.80 0.7H, *dd*	7.78 0.3H, *dd*
H_2-7′	3.26 1.4H, *br d* (7)	3.19 0.6H, *br d*	3.27 1.2H, *br d*	3.19 0.8H, *br d*	3.06–3.25 (2H, *m*)†		6.38 0.7H, *d*	6.36 0.3H, *d*
8′	5.32 0.7H, *br t* (7)	5.24 0.3H, *br t*	5.32 0.6H, *br t*	5.24 0.4H, *br t*	4.74 *dd* (7.5 and 9)	4.75 0.4H, *dd*	5.69 0.7H, *d*	5.68 0.3H, *d*
Me-9′	1.60, 1.61 and 1.72 total 6H, each *br s*		1.63, 1.62 and 1.71 total 6H, each *br s*		1.21, 1.26 and 1.28 total 6H, each *s*		1.42 4.2H, *s*	1.41 1.8H, *s*
7″	2.8–2.9 2H,* *m*		3.38 1.2H, *br d*	3.35 0.8H, *br d*	3.37 1.2H, *br d* (7)	3.34 0.8H, *br d*	3.37 1.4H, *br d*	3.34 0.6H, *br d*
8″	4.4–4.45 1H, *m*		5.36 0.6H, *br t*	5.34 0.4H, *br t*	5.35 0.6H, *br t* (7)	5.33 0.4H, *br t*	5.35 0.7H, *br t*	5.32 0.4H, *br t*
Me-9″	1.82 2.1H, *br s*	1.78 0.9H, *br s*	1.74 and 1.75 total 6H, each *br s*		1.69, 1.72 and 1.74 total 6H, each *br s*		1.68, 1.72 and 1.73 total 6H, each *br s*	
11″	4.79 0.7H, *br s*	4.76 0.3H, *br s*						
	4.98 0.7H, *br s*	4.94 0.3H, *br s*						
OH-3	15.76 0.7H, *br s*		15.78 0.6H, *br s*		15.67 0.6H, *br s*		15.69 0.7H, *br s*	
OH-2′	12.25 0.7H, *br s*	12.36 0.3H, *s*	12.25 0.6H, *s*	12.36 0.4H, *s*	12.69 0.6H, *br s*	12.83 0.4H, *s*	12.49 0.7H, *br s*	12.55 0.3H, *s*

*In $CDCl_3$; (enol form): δ2.89 (0.7H, *dd*, J = 2 and 14 Hz), 3.05 (0.7H, *ddd*, J = 9 and 14 Hz), (keto form): 2.88 (0.3H, *dd*, J = 2 and 14 Hz), 3.00 (0.3H, *dd*, J = 9 and 14 Hz).
†When the signals of H-8′ were irradiated (decoupling mode), the signals of H_2-7′ changed to broad doublet signals [δ3.18 and 3.22 (each 1H, J = 16 Hz)].



δ15.67 (0.6H, *br s*, OH-3 of β-hydroxychalcone form). These signals (H-2 and the hydroxyl protons) disappeared on the addition of methanol-d_4, as described in the case of **1**. All other signals, i.e. the signals of protons of a prenyl group, a 2(1-hydroxy-1-methylethyl)-2,3-dihydrofuran ring, a singlet and a broad triplet (J = 1 Hz) aromatic protons (A ring) and ABX-type aromatic protons (B ring), appeared as pairs arising from the two tautomeric structures. The chemical shifts of the B ring protons and protons of the prenyl group of **2** resembled those of glyinflanin C (**9**) [5]. The mass spectrum showed characteristic fragment ions at m/z 221 (**2a**, A ring) and 189 (**2b**, B ring). From the above data, it was suggested that the dihydrofuran was on the A ring and the prenyl group on the B ring. The presence of the dihydrofuran ring on the A ring was confirmed by the following decoupling experiment. When the signals of C-7'-H × 2 (δ3.13) were irradiated, the broad triplet signals at δ7.72 and 7.87 (J = 1 Hz, C-6'-H) changed to singlet signals. Thus, the structures of the keto and enol forms of glyinflanin F were elucidated as **2** and **2'**, respectively, except for the stereochemistry at the C-8' position.

Glyinflanin G (**3**), $C_{25}H_{24}O_5$, gave a brown colour with the methanolic ferric chloride test on a TLC plate. The ^{1}H NMR spectrum ($CDCl_3$) indicated that the compound was a 2'-hydroxychalcone derivative [δ7.40 (*d*, J = 15 Hz, H-α), 7.76 (*d*, J = 15 Hz, H-β) and 13.77 (*s*, OH-2')]. The ^{1}H NMR spectrum of **3** (acetone-d_6) showed the signals of *ortho*-coupled aromatic protons (A ring), *meta*-coupled aromatic protons (B ring) and protons of two 2,2-



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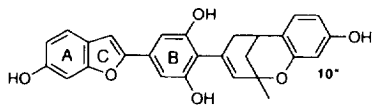

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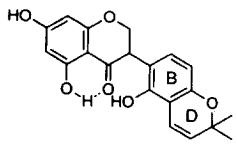

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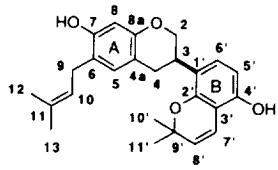

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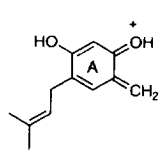

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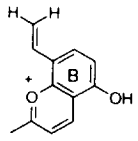

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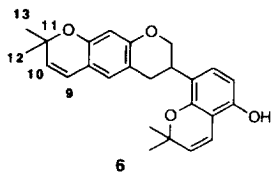

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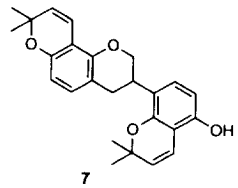

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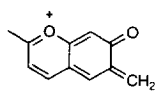

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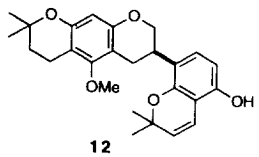

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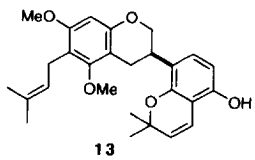

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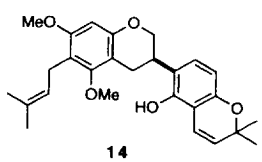

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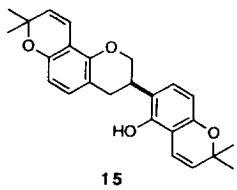

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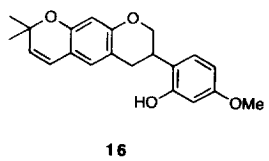

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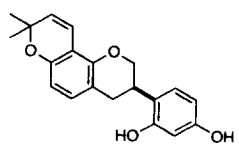

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dimethylpyran rings. The mass spectrum showed characteristic fragment ions at *m/z* 203 (**3a**, A ring) and 187 (**3b** and **c**, A and B rings) indicating that the pyran rings were located at both A and B rings. The chemical shift of the H-7 (δ6.36, the olefinic proton of one of the pyran rings) indicated the absence of a hydroxyl group at the *peri*-position of H-7 [12]. These data indicated that the partial structure of the B ring is **3d**, **e** or **f**. The structure was elucidated with the following NOE experiment (acetone-d_6). When the signal of H-α and H-β [δ7.77 (2H, *s*)] was irradiated, enhancements were observed at H-2 (9%), H-6 (5%) and H-6′ (8%). Thus, the structure of glyinflanin G is **3**.

Glyinflanin H (**4**), $C_{19}H_{16}O_4$, was negative to the ferric chloride test on a TLC plate. The UV spectrum resembled that of 2-arylbenzofuran derivatives [13]. The ^{1}H NMR spectrum of **4** showed signals of AMNX-type olefinic and aromatic protons (H-3 and A ring), *ortho*-coupling aromatic protons (AX-type, B ring) and protons of a 2,2-dimethylpyran ring. The spin networks of the aromatic proton signals were confirmed by a ^{1}H–^{1}H COSY spectrum. The structure of the B ring was deduced by the presence of zigzag coupling (J = 0.7 Hz) between H-5′ and H-7′. These data suggested that the structure of glyinflanin H is **4**. The chemical shifts of the carbons of **4** were observed with its HMBC and complete decoupling spectra as shown in Table 2. The chemical shifts of the A and C rings resembled those of mulberrofuran H (**10**) [14], except C-2 and those of the B and D rings were similar to those of licoisoflavanone (**11**) [8], except for C-1′. From these data, the structure of glyinflanin H is characterized as **4**.

Glyinflanin I (**5**), $C_{25}H_{28}O_4$, was negative to the methanolic ferric chloride test on a TLC plate. The UV spectrum indicated that the compound is a flavan or an isoflavan. The ^{1}H NMR spectrum of **5** (acetone-d_6) showed the characteristic signals of an isoflavan derivative [δ3.92 (*t*, H-2), 4.14 (*ddd*, H-2), 3.40 (*m*, H-3), 2.72 (*br ddd*, H-4) and 2.90 (*br dd*, H-4)]. The spectrum also showed signals of two singlet aromatic protons (A ring), *ortho*-

Table 2. ^{13}C NMR spectral data of compounds **4–6**, **10–12** and **16** (in acetone-d_6, 100 or 125 MHz)

C	4	10	11	C	5	12	6	16
2	(153.4)*	155.3		2	70.7		70.6	70.6
3	104.1	103.9†		3	32.9		32.6	32.6
3a	(123.1)	122.4		4	31.4		31.0	31.0
4	121.7	121.9		4a	114.2		115.6	115.6
5	113.1	113.2		5	131.2		128.0	128.0
6	156.9	156.7		6	121.3		115.5	115.6
7	98.5	98.4		7	154.2		156.0	156.1
7a	(156.1)	156.7		8	103.7		104.6	104.6
1′	(113.0)		116.3	8a	154.9		153.3	153.3
2′	(150.6)		151.6	9	28.7		122.7	122.8
3′	(111.5)		111.4	10	124.9		129.0	129.0
4′	(155.0)		154.2	11	131.2		76.5	76.6
5′	110.0		109.4	12	18.0		28.1	28.1
6′	130.5		130.1	13	26.1		28.1	28.2
7′	117.4		117.4	1′	121.2	121.0	120.6	
8′	127.8		129.9	2′	152.3	152.8	152.8	
9′	76.6		76.0	3′	110.5	110.4	110.3	
10′, 11′	28.1		27.8	4′	153.0	153.2	153.5	
				5′	108.6	108.7	108.4	
				6′	128.1	127.9	127.9	
				7′	118.3	118.1	118.0	
				8′	129.4	129.3	129.3	
				9′	76.7	76.5	76.5	
				10′, 11′	28.1	27.9	27.8, 27.9	

* Signals shown in parentheses were not observed in the complete decoupling spectrum of **4** because of a limitation in the quantity of the available sample. The figures in parentheses are the chemical shift of the cross-peak in its HMBC spectrum.

†Signal reassigned with C-10″.

coupled aromatic protons (AX-type, B ring), protons of a prenyl group, protons of a 2,2-dimethylpyran ring and two hydroxyl protons. One of the singlet aromatic protons [δ6.75 (C-5-H)] was observed as a broad singlet signal (triplet-like) owing to four-bond coupling with H-4 × 2 (confirmed with a decoupling experiment) [10]. The mass spectrum showed characteristic fragment ions at *m/z* 191 (**5a**, A ring) and 187 (**5b**, B ring). The chemical shifts of the B ring and the 2,2-dimethylpyran ring protons resembled those of kanzonols J (**12**) and I (**13**),

Table 3. ^{1}H NMR spectral data of compounds **6**, **7**, **16** and **17** (in acetone-d_6)

H	6	7	16	17
2	3.93 *t* (10)	4.02 *t* (10)	4.01 *t* (10)	4.00 *t* (10)
	4.19 *ddd* (2, 5 and 10)	4.27 *ddd* (2, 3.5 and 10)	4.25 *ddd* (2, 3 and 10)	4.32 *ddd* (2, 3 and 10)
3	3.41 *m*	3.42 *m*	3.44 *m*	3.45 *m*
4	2.75 *br ddd* (2, 5 and 15.5)	2.76 *br ddd* (2, 5 and 15.5)	2.81 *br ddd* (2, 5 and 15)	2.97 *dddd* (1, 2, 11 and 16)
	2.93 *ddd* (0.7, 11 and 15.5)	2.95 *ddd* (1, 11 and 15.5)	2.97 *ddd* (1, 10 and 15)	2.77 *dddd* (0.5, 2, 5 and 16)
5	6.73 *br s*	6.82 *br d* (8)	6.73 *br s*	6.82 *br d* (8)
6	—	6.28 *dd* (0.5 and 8)	—	6.27 *dd* (0.7 and 8)
8	6.16 *br s*	—	6.17 *br s*	—
9	6.30 *br d*	6.61 *dd* (0.5 and 10)	6.29 *br d* (10)	6.60 *dd* (0.7 and 10)
10	5.55 *d* (10)	5.62 *d* (10)	5.54 *d* (10)	5.60 *d* (10)
Me-11	1.36 6H, *s*	1.36, 1.37 each 3H, *s*	1.36 6h, *s*	1.35, 1.37 each 3H, *s*
5′	6.39 *d* (8)	6.40 *d* (8.5)		
6′	6.86 *d* (8)	6.87 *d* (8.5)		
7′	6.69 *d* (10)	6.69 *d* (10)		
8′	5.65 *d* (10)	5.65 *d* (10)		
Me-9′	1.41, 1.42 each 3H, *s*	1.41, 1.42 each 3H, *s*		
OH	8.41 *s*	8.45 *s*		

rather than those of **14** [15]. In the ^{13}C NMR spectrum of **5** (Table 2), the chemical shifts of the B ring and the 2,2-dimethylpyran ring resembled those of **12**. The absolute configuration of **5** was assigned as 3*R* from its CD spectrum, in which a positive Cotton effect exhibited at the ^1L_b-band [284 nm (sh)] [15].* From these data, the structure of glyinflanin I is assigned to be **5**.

Glyinflanins J (**6**) and K (**7**), $C_{25}H_{26}O_4$, were dipyranoisoflavans and structural isomers of hispaglabridin B (**15**) isolated from *G. glabra* var. *typica* (Spanish licorice) [16]. The NMR spectra of **6** and **7** (Tables 2 and 3) indicated that the substitution pattern of the B rings of these compounds is the same as glyinflanin I (**5**). The B ring structure of **7** was further confirmed by a NOE experiment. When the signal of the OH-4′ (δ8.45) was irradiated, an enhancement was observed at H-5′ (16%). In the ^1H and ^{13}C NMR spectra of **6**, the chemical shifts and coupling patterns of the A ring and the other 2,2-dimethylpyran ring were similar to those of gancaonin X (**16**) [10]. On the other hand, the chemical shifts and coupling patterns of the A ring and the other 2,2-dimethylpyran ring protons of **7** were similar to those of glabridin (**17**) isolated from *G. glabra* (Russian licorice) [17]. Thus, the structures of glyinflanins J and K are **6** and **7**, respectively.

EXPERIMENTAL

General procedures were followed and the instruments used are described in our previous paper [10]. UV and CD spectra were measured in MeOH. Plant materials, extraction and CC of the extract are as reported in the preceding paper [5]. A voucher specimen is deposited in the drug museum of the Department of Pharmacognosy, School of Pharmaceutical Sciences, Beijing Medical University, P.R. China. The known compounds, isoderrone (1 mg), licoisoflavone B (4 mg), 8-(γ,γ-dimethylallyl)-wighteone (3 mg), gancaonin Z (0.3 mg) and phaseollin (1 mg) were isolated from the roots of *Glycyrrhiza inflata* (2 kg) in the course of the isolation of the following new compounds. The known compounds were identified by direct comparison with authentic samples or from their spectral data.

Isolation of isoprenoid-substituted flavonoids (**1**–**7**). Powdered roots of *G. inflata* (2 kg) were extracted with EtOH. The EtOH extract (200 g) was absorbed on Amberlite XAD-2 resin and washed with H_2O and organic solvents [5]. The C_6H_6 eluent (17 g) was subject to silica gel CC. Fr. 8 from the column (370 mg), which was described in the preceding paper [5], was purified by prep. TLC ($CHCl_3$–Me_2CO, 10:1; hexane–EtOAc, 2:1, developed 3×; hexane–Et_2O, 2:1, 3×; hexane–Me_2CO, 3:1; $CHCl_3$ only, 3×; C_6H_6–Me_2CO, 5:1; $CHCl_3$–MeOH, 50:1) to give glyinflanins E (**1**, 0.1 mg), F (**2**, 0.4 mg), G (**3**, 0.2 mg), H (**4**, 0.5 mg) and I (**5**, 0.7 mg). Fr. 4 from the column (130 mg) was purified by prep. TLC C_6H_6–$CHCl_3$, 2:1; hexane–EtOAc, 6:1; 2×; $CHCl_3$–hexane, 2:1; C_6H_6–MeOH–28% NH_3–H_2O, 120:3:1) to give glyinflanin J (**6**, 1.4 mg) and glyinflanin K (**7**, 0.5 mg).

Glyinflanin E (**1**). Yellow powder. UV λ_{max} nm (log ε): 208 (4.75), 230 (sh 4.50), 285 (4.35), 338 (4.09), 386 (4.33), 395 (sh 4.31). EI-MS (probe) 70 eV, *m/z* (rel. int.): 425 [M + 1]$^+$ (5%), 424 [M]$^+$ (15), 406 (4), 356 (14), 354 (18), 337 (23), 205 (100), 187 (47). HR-MS *m/z*: 424.1887 [M]$^+$ ($C_{25}H_{28}O_6$ requires: 424.1886), 205.0849 [**1a** and **1b**] ($C_{12}H_{13}O_3$ requires: 205.0865). NOE experiment (Me_2CO-d_6): when the signal at δ3.26 was irradiated, enhancements were observed at δ1.72 (*br s*, 1.5%), 5.32 (*br t*, 4.5%) and 7.77 (*s*, 4%). CD (*c* 0.0024 g/100 ml): $[\theta]_{227}$ 0, $[\theta]_{240}$ − 3300, $[\theta]_{270}$ − 2100 (sh), $[\theta]_{293}$ − 3200, $[\theta]_{333}$ 0, $[\theta]_{382}$ − 390, $[\theta]_{455}$ − 750, $[\theta]_{526}$ 0.

Glyinflanin F (**2**). Yellow powder. UV λ_{max} nm (log ε): 204 (4.91), 220 (sh 4.74), 230 (sh 4.66), 283 (4.51), 334 (4.39), 387 (4.56), 400 (sh 4.55). EI-MS *m/z* (rel. int.): 425 [M + 1]$^+$ (3), 424 [M]$^+$ (11), 407 (1), 221 (9), 189 (56). HR-MS *m/z*: 424.1883 [M]$^+$ ($C_{25}H_{28}O_6$ requires: 424.1886), 221.0810 (**2a**) ($C_{12}H_{13}O_4$ requires: 221.0814), 189.0920 (**2b**) ($C_{12}H_{13}O_2$ requires: 189.0916). ^{13}C NMR (125 MHz, Me_2CO-d_6): (enol form); δ17.9 (C-10″), 25.5, 26.03 (C-10′ and C-11′), 25.9 (C-11″), 29.2 (C-7″), 30.6 (C-7′), 71.39 (C-9′), 91.1 (C-2), 92.31 (C-8′), 98.4 (C-3′), 112.8 (C-1′), 116.0 (C-5″), 121.5 (C-5′), 123.2 (C-8″), 126.0 (C-6′), 126.2 (C-1″), 127.4 (C-6″), 129.2 (C-3″), 129.5 (C-2″), 133.0 (C-9″), 160.1 (C-4″), 177.6 (C-3), 194.8 (C-1), (keto form); δ17.8 (C-10″), 25.6, 25.95 (C-10′ and C-11′), 25.8 (C-11″), 30.4 (C-7′), 49.9 (C-2), 71.36 (C-9′), 92.5 (C-8′), 97.9 (C-3′), 115.6 (C-5″), 121.2 (C-5′), 122.8 (C-8″), 129.6 (C-3″ and C-6″), 129.7 (C-6′), 130.6 (C-1″), 131.5 (C-2″), 133.0 (C-9″), 160.9 (C-4″), 193.8 (C-3), 200.4 (C-1). CD (*c* 0.003): $[\theta]_{230}$ 0, $[\theta]_{240}$ − 430, $[\theta]_{255}$ 0, $[\theta]_{295}$ − 700, $[\theta]_{325}$ 0.

Glyinflanin G (**3**). Yellow powder. UV λ_{max} nm (log ε): 206 (4.25), 270 (3.81), 385 (3.37). EI-MS (3.37) *m/z* (rel. int.): 405 [M + 1]$^+$ (3), 404 [M]$^+$ (20), 389 (30), 203 (24), 187 (72). HR-MS *m/z*: 404.1605 [M]$^+$ ($C_{25}H_{24}O_5$ requires: 404.1624). ^1H NMR (400 MHz, $CDCl_3$): δ1.44, 1.50 (each 6H, *s*, Me × 4), 5.59 (1H, *d*, *J* = 10 Hz, H-8′), 5.68 (1H, *d*, *J* = 10 Hz, H-8), 6.36 (1H, *d*, *J* = 10 Hz, H-7), 6.38 (1H, *br d*, *J* = 9 Hz, H-5′), 6.75 (1H, *dd*, *J* = 0.6 and 10 Hz, H-7′), 6.88 (1H, *d*, *J* = 2 Hz, C-2), 7.14 (1H, *d*, *J* = 2 Hz, H-6), 7.40 (1H, *d*, *J* = 15 Hz, H-α), 7.71 (1H, *d*, *J* = 9 Hz, H-6′), 7.76 (1H, *d*, *J* = 15 Hz, H-β), 13.77 (1H, *s*, 2′-OH); (400 MHz, Me_2CO-d_6): δ1.44 (12H, *s*, Me × 4), 5.72 (1H, *d*, *J* = 10 Hz, H-8′), 5.81 (1H, *d*, *J* = 10 Hz, H-8), 6.37 (1H, *dd*, *J* = 0.5 and 9 Hz, H-5′), 6.44 (1H, *d*, *J* = 10 Hz, H-7), 6.70 (1H, *dd*, *J* = 0.5 and 10 Hz, H-7′), 7.10 (1H, *d*, *J* = 2 Hz, H-2), 7.28 (1H, *d*, *J* = 2 Hz, H-6), 7.77 (2H, *s*, H-α and H-β), 8.09 (1H, *d*, *J* = 9 Hz, H-6′), 14.04 (1H, *s*, OH-2′).

Glyinflanin H (**4**). Amorphous powder. UV λ_{max} nm (log ε): 210 (4.40), 225 (sh 4.24), 278 (4.22), 290 (sh 4.13), 310 (sh 4.13), 320 (4.19), 350 (sh 3.68). EI-MS *m/z* (rel. int.):

*We reported that the Cotton effects at ^1L_b-band of kanzonol I (**13**) and **14**, both derived from licorisoflavan A [(*R*)-2′,4′-dihydroxy-5,7-dimethoxy-6,3′-diprenylisoflavan], were different from each other in their CD spectra (**13**: positive Cotton effect, **14**: negative Cotton effect) [15]. The CD spectral study of the other type pyranoisoflavans having a pyran ring at the A ring is now in progress.

309 $[M + 1]^+$ (8), 308 $[M]^+$ (38), 293 (100), 149 (77), 111 (17). HR-MS *m/z*: 308.1061 $[M]^+$ ($C_{19}H_{16}O_4$ requires: 308.1049). ^{1}H NMR (400 MHz, Me_2CO-d_6): δ1.40 (6H, *s*, Me × 2), 5.74 (1H, *d*, *J* = 10 Hz, H-8′), 6.45 (1H, *dd*, *J* = 0.7 and 8.5 Hz, H-5′), 6.78 (1H, *dd*, *J* = 2 and 8.5 Hz, H-5), 6.83 (1H, *dd*, *J* = 0.7 and 10 Hz, H-7′), 6.99 (1H, *dd*, *J* = 0.9 and 2 Hz, H-7), 7.09 (1H, *d*, *J* = 0.9 Hz, H-3), 7.37 (1H, *d*, *J* = 8.5 Hz, H-4), 7.54 (1H, *d*, *J* = 8.5 Hz, H-6′).

Glyinflanin I (**5**). Amorphous powder. $[\alpha]_D$ + 88° (MeOH; *c* 0.0023). UV λ_{max} nm (log ε): 210 (4.43), 225 (sh 4.39), 284 (3.88), 320 (sh 3.17). EI-MS *m/z* (rel. int.): 393 $[M + 1]^+$ (7), 392 $[M]^+$ (22), 377 (21), 337 (2), 191 (13), 190 (18), 187 (38), 175 (17), 161 (13), 149 (32), 69 (100). HR-MS *m/z*: 392.2000 $[M]^+$ ($C_{25}H_{28}O_4$ requires: 392.1988). ^{1}H NMR (400 MHz, Me_2CO-d_6): δ1.40, 1.42 (each 3H, *s*, Me-9′ × 2), 1.69 (6H, *br d*, *J* = 1 Hz, Me_2-11), 2.72 (1H, *br ddd*, *J* = 2, 6 and 16 Hz, H-4), 2.90 (1H, *br dd*, *J* = 11 and 16 Hz, H-4), 3.21 (2H, *br d*, *J* = 7 Hz, H_2-9), 3.40 (1H, *m*, H-3), 3.92 (1H, *t*, *J* = 10 Hz, H-2), 4.14 (1H, *ddd*, *J* = 2, 4 and 10 Hz, H-2), 5.30 (1H, *m*, H-10), 5.64 (1H, *d*, *J* = 10 Hz, H-8′), 6.29 (1H, *s*, H-8), 6.38 (1H, *d*, *J* = 8 Hz, H-5′), 6.69 (1H, *d*, *J* = 10 Hz, H-7′), 6.75 (1H, *br s*, H-5), 6.85 (1H, *d*, *J* = 8 Hz, H-6′), 8.03 (1H, *br s*, 7-OH), 8.44 (1H, *br s*, OH-4′). CD (*c* 0.0084): $[\theta]_{209}$ 0, $[\theta]_{214}$ + 9100, $[\theta]_{226}$ 0, $[\theta]_{236}$ − 7900, $[\theta]_{249}$ 0, $[\theta]_{284}$ + 1800 (sh), $[\theta]_{293}$ + 3200, $[\theta]_{340}$ 0.

Glyinflanin J (**6**). Amorphous powder. $[\alpha]_D$ + 86° (MeOH; *c* 0.0058). UV λ_{max} nm (log ε): 224 (4.19), 235 (sh 4.05), 277 (3.64), 285 (sh 3.61), 311 (3.42), 320 (sh 3.36). EI-MS *m/z* (rel. int.): 391 $[M + 1]^+$ (11), 390 $[M]^+$ (31), 375 (100), 202 (2), 187 (**5b**) (27), 189 (11), 174 (7), 173 (**6a**) (18). HR-MS *m/z*: 390.1799 $[M]^+$ ($C_{25}H_{26}O_4$ requires: 390.1831). CD (*c* 0.0029): $[\theta]_{220}$ 0, $[\theta]_{225}$ + 88000, $[\theta]_{234}$ 0, $[\theta]_{236}$ − 5400, $[\theta]_{239}$ 0, $[\theta]_{244}$ + 11000, $[\theta]_{287}$ + 3500, $[\theta]_{314}$ + 2500 (sh), $[\theta]_{375}$ 0.

Glyinflanin K (**7**). Amorphous powder. $[\alpha]_D$ + 49° (MeOH; *c* 0.0041). UV λ_{max} nm (log ε): 204 (4.39), 223 (4.54), 279 (4.08), 290 (sh 4.02), 310 (sh 2.56). EI-MS *m/z* (rel. int.): 391 $[M + 1]^+$ (12), 390 $[M]^+$ (33), 375 (100), 187 (**5b**) (85), 173 (94). HR-MS *m/z*: 390.1811 $[M]^+$ ($C_{25}H_{26}O_4$ requires: 390.1831). ^{1}H NMR (400 MHz, $CDCl_3$): δ1.41, 1.42, 1.43, 1.44 (each 3H, *s*, Me), 2.81 (1H, *br ddd*, *J* = 2, 5 and 16 Hz, H-4), 2.95 (1H, *ddd*, *J* = 1, 11 and 16 Hz, H-4), 3.50 (1H, *m*, H-3), 4.02 (1H, *t*, *J* = 10 Hz, H-2), 4.33 (1H, *ddd*, *J* = 2, 3.5 and 10 Hz, H-2), 5.56 (1H, *d*, *J* = 10 Hz, H-10), 5.61 (1H, *d*, *J* = 10 Hz, H-8′), 6.28 (1H, *d*, *J* = 8 Hz, H-5′), 6.36 (1H, *dd*, *J* = 0.5 and 8 Hz, H-6), 6.63 (1H, *d*, *J* = 10 Hz, H-7′), 6.67 (1H, *dd*, *J* = 0.5 and 10 Hz, H-9), 6.80 (1H, *d*, *J* = 8 Hz, H-6′), 6.82 (1H, *br d*, *J* = 8 Hz, H-5). CD (*c* 0.0051): $[\theta]_{233}$ 0, $[\theta]_{237}$ − 18000, $[\theta]_{252}$ 0, $[\theta]_{268}$ + 2600, $[\theta]_{276}$ 0, $[\theta]_{284}$ − 10000 (sh), $[\theta]_{293}$ − 13000, $[\theta]_{316}$ 0, $[\theta]_{328}$ + 1400, $[\theta]_{361}$ 0.

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