# Chemical Studies of Chinese Licorice-Roots. I. Elucidation of Five New Flavonoid Constituents from the Roots of *Glycyrrhiza glabra* L. Collected in Xinjiang

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Received December 13, 1993; accepted January 18, 1994

**From the air-dried roots of *Glycyrrhiza glabra* L. (Leguminosae) collected in Xinjiang province, China ("Shinkyo-Kanzo" in Japanese), five new flavonoid compounds named glucoliquiritin apioside (1) (a flavanone bisdesmoside), prenyllicoflavone A (5) (a bisprenylflavone), shinflavanone (7) (a prenylated pyranoflavanone), shinpterocarpin (9) and 1-methoxyphaseollin (12) (both pyranopterocarpans), were isolated together with eight known saponins, seven known flavonoid glycosides, and eleven flavonoids. The structures of the new compounds have been elucidated on the basis of their chemical and physicochemical properties.**

**Keywords** *Glycyrrhiza glabra*; Leguminosae; licorice root; flavonoid bisdesmoside; flavonoid prenylated; pyranopterocarpan

During the course of our chemical studies on the constituents of various botanically identified Chinese licorice-roots, we reported the isolation and structure elucidation of ten then-new oleanene-type triterpene oligoglycosides[1] (named licorice-saponins A3, B2, C2, D3, E2, F3, G2, H2, J2, and K2) from the air-dried roots of *Glycyrrhiza uralensis* FISCHER, which were collected in the northeast area of China. These roots usually occupy the major part of "Tohoku-Kanzo (東北甘草)" imported from China in Japan.

Successively, we investigated the chemical constituents of several licorice-roots which were collected in Xinjiang province, China. They are usually imported in Japan under the name of "Shinkyo-Kanzo (新疆甘草)". We reported the isolation and structure elucidation of apioglycyrrhizin and araboglycyrrhizin, two then-new sweet oleanene-type triterpene oligoglycosides,[2] from a Xinjiang licorice-root, which was botanically identified as *Glycyrrhiza inflata* BATALIN. We then reported the structure elucidation of a new oleanene-type triterpene oligoglycoside named licorice-saponin L3,[3] and a new flavonoid glycoside named isoliquiritin apioside,[3] isolated from the air-dried roots of *Glycyrrhiza uralensis* FISCHER, collected in Xinjiang province.

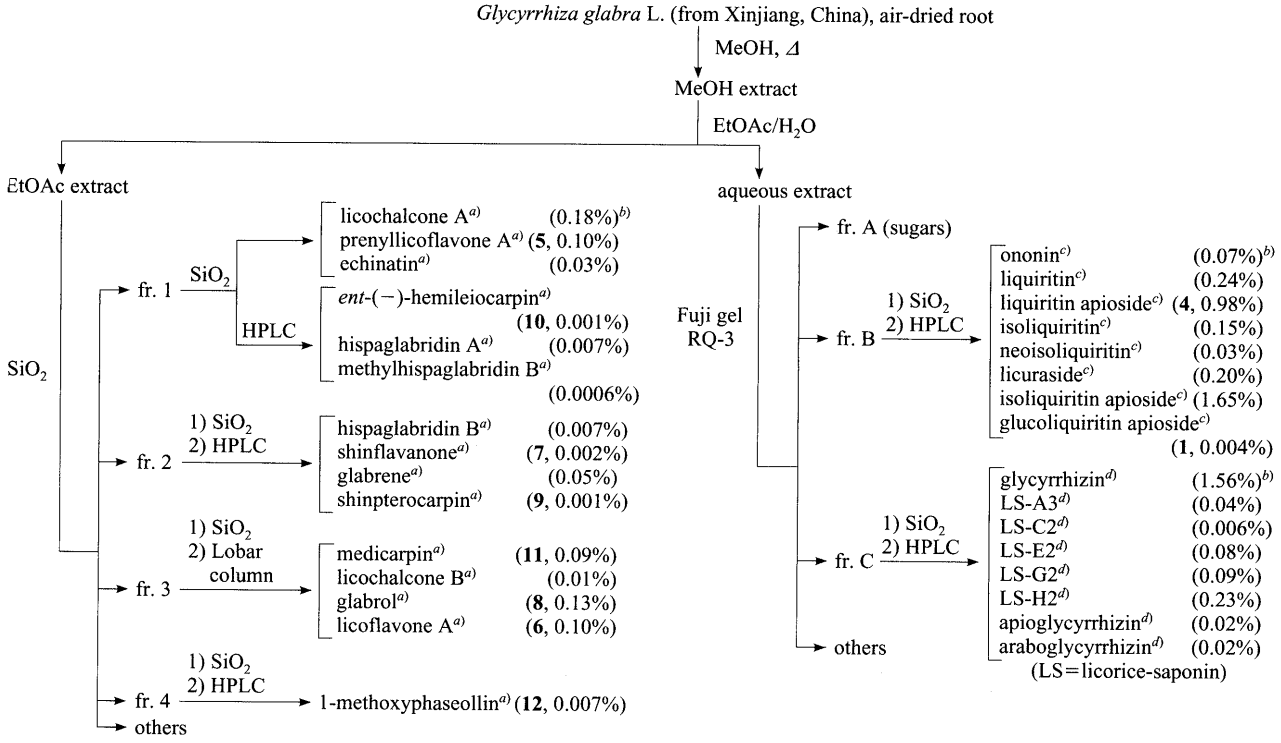
As a continuation of these investigations, we have isolated five new flavonoid constituents from the air-dried roots of *Glycyrrhiza glabra* L., collected in Xinjiang province of China.[4] They are a flavone bisdesmoside named glucoliquiritin apioside (**1**), a bisprenylflavone named prenyllicoflavone A (**5**), a prenylated pyranoflavanone named shinflavanone (**7**), and two pyranopterocarpans named shinpterocarpin (**9**) and 1-methoxyphaseollin (**12**). This paper presents a full account of the structure elucidation of these flavonoids.

The isolation of the chemical constituents from the air-dried roots of *Glycyrrhiza glabra* L. was carried out through the procedure shown in Fig. 1.

The methanolic extract of the roots was partitioned into an ethyl acetate and water mixture. The water-soluble portion (aqueous extract) was subjected to reversed-phase silica gel column chromatography to provide the sugar fraction (fr. A) and the glycoside fractions (fr. B and fr. C). Repeated separation of the glycoside fractions by means of ordinary-phase silica gel column chromatography and subsequent high-performance liquid chromatography (HPLC) furnished eight known saponins from fr. C (glycyrrhizin, licorice-saponins A3, C2, E2, G2, H2,[1] apioglycyrrhizin, and araboglycyrrhizin[2]), and a new flavanone bisdesmoside named glucoliquiritin apioside (**1**) from fr. B, together with seven known flavonoid glycosides [ononin,[5] liquiritin,[6] liquiritin apioside (**4**),[3] isoliquiritin,[3] neoisoliquiritin,[3] licuraside,[3] and isoliquiritin apioside[3]].

On the other hand, the ethyl acetate-soluble portion (EtOAc extract) was subjected to ordinary-phase silica gel column chromatography repeatedly, followed by HPLC to furnish three known chalcones (licochalcones A[7] and B,[7] and echinatin[7]), two new prenylated flavonoids [prenyllicoflavone A (**5**)[8,9] and shinflavanone (**7**)], together with two known prenylated flavonoids [glabrol (**8**),[10] licoflavone A (**6**)[11]], three known isoflavonoids (hispaglabridins A[12] and B,[12] and methylhispaglabridin B[12,13]), two new pyranopterocarpans [shinpterocarpin (**9**) and 1-methoxyphaseollin (**12**)], and two known pterocarpans [medicarpin (**11**)[14] and *ent*-(−)-hemileiocarpin (**10**)[15,16]].

**Glucoliquiritin Apioside (1)** Glucoliquiritin apioside (**1**) was obtained as pale yellow prisms of mp 157—158 °C. The molecular formula, $C_{32}H_{40}O_{18}$, was determined from the *quasi*-molecular ion peak observed at *m/z* 735.2075 [$(M+H)^+$] by high-resolution fast atom bombardment mass spectrum (FAB-MS) analysis. The proton magnetic resonance ($^1$H-NMR) spectrum of **1** showed three anomeric proton signals [$\delta$ 4.92 (1H, d, $J$=7.3 Hz), 4.97 (1H, d, $J$=7.0 Hz), and 5.36 (1H, br s)], which suggested **1** to be a triglycoside.




*a*) flavonoid, *b*) isolated yield from the air-dried roots, *c*) flavonoid glycoside, *d*) saponin

Fig. 1

Methanolysis of glucoliquiritin apioside (**1**) with 9% hydrogen chloride in methanol yielded isoliquiritigenin (**2**) and (±)-liquiritigenin (**3**) together with methyl D-glucoside and methyl D-apioside in 2:1 ratio as determined by gas-liquid chromatographic (GLC) analysis. The two methyl glycosides thus liberated were further subjected to acidic hydrolysis to furnish D-glucose and D-apiose, respectively. The $^{13}$C-NMR spectrum of **1** showed the carbon signals assignable to a liquiritigenin (**3**) moiety, a β-D-glucopyranosyl moiety, and a β-D-apiofuranosyl(1→2)-β-D-glucopyranosyl moiety. The presence of the β-D-apiofuranosyl structure in **1** was presumed from the chemical shift of the apiosyl anomeric carbon, which was observed at $\delta_C$ 109.0 ppm[1b,17] (Table I).

In order to elucidate the location of two sugar moieties (one glucose and one 2-apiosylglucose), glucoliquiritin apioside (**1**) was subjected to enzymatic partial hydrolysis. Thus, treatment of **1** with snail enzyme[18] gave a known flavanone glycoside, liquiritin apioside (**4**). This finding led us to conclude that the compound **1** is a 7-*O*-glucopyranoside of liquiritin apioside (**4**).[3] Finally, the absolute configuration at C-2 of **1** was demonstrated to be *S* on the basis of the circular dichroism (CD) analysis[19] of **1**: $[\theta]_{330}$ $+9.7\times10^3$ (positive maximum) due to n→π* transition, $[\theta]_{287}$ $-1.1\times10^4$ (negative maximum) due to π→π* transition. Consequently, the structure of gluco-liquiritin apioside can be expressed as 4′-*O*-β-D-apiofuranosyl(1‴→2‴)-β-D-glucopyranosyl-7-*O*-β-D-glucopyranosylliquiritigenin (**1**).

**Prenyllicoflavone A (5)** Prenyllicoflavone A (**5**) was isolated as a yellowish oily compound. From the high-resolution electron impact mass spectrum (EI-MS), the molecular composition of **5** was determined as $C_{25}H_{26}O_4$. Detailed comparison of the $^1$H-NMR and $^{13}$C-NMR data for **5** with those for a known prenylflavonoid licoflavone A (**6**),[11] suggested that compound **5** is a C-6 prenylated analogue of **6** (Table II). Thus, the characteristic signals due to the protons on a 1,2,4-trisubstituted benzene ring of **5** were observed at δ 7.01 (1H, d, $J$=8.6 Hz), 7.72 (1H, dd, $J$=2.1, 8.6 Hz), and 7.78 (1H, d, $J$=2.1 Hz), as for **6**. Moreover, correlation spectroscopy *via* long-range coupling (COLOC) experiments on **5** revealed correlations between the four-proton signal at δ 3.41 (1″-$H_2$ and 1‴-$H_2$) and the carbon signals at $\delta_C$ 126.2 (C-2′), 129.7 (C-3′), 159.2 (C-4′), 126.1 (C-5), 128.5 (C-6), and 164.0 (C-7), between the one-proton signal at δ 7.78 (2′-H) and the carbon signal at $\delta_C$ 29.0 (C-1‴), and between the one-proton signal at δ 7.82 (5-H) and the carbon signal at $\delta_C$ 28.6 (C-1″).

Consequently, the chemical structure of prenyllicoflavone A is 6,3′-bis(3‴,3‴′-dimethylallyl)-7,4′-dihydroxyflavone (**5**).

**Shinflavanone (7)** Shinflavanone (**7**) was isolated as a yellowish oily compound. The molecular composition was defined as $C_{25}H_{26}O_4$ from the high-resolution EI-MS analysis. This compound showed the ultraviolet (UV) absorption maxima at 238 (ε=18000) and 275 nm (ε=11000), which were ascribable to the flavanone skeleton. The $^1$H-NMR spectrum of **7** showed the signals of a typical $A_2B$ pattern at δ 2.80 (1H, dd, $J$=3.0, 16.6 Hz), 3.01 (1H, dd, $J$=13.2, 16.6 Hz), and 5.38 (1H, dd, $J$=3.0, 13.2 Hz), which were assignable to 3-$H_2$ and 2-H in the flavanone skeleton. Furthermore, three aromatic proton signals observed at δ 6.85 (1H, d, $J$=8.3 Hz), δ 7.20 (1H,

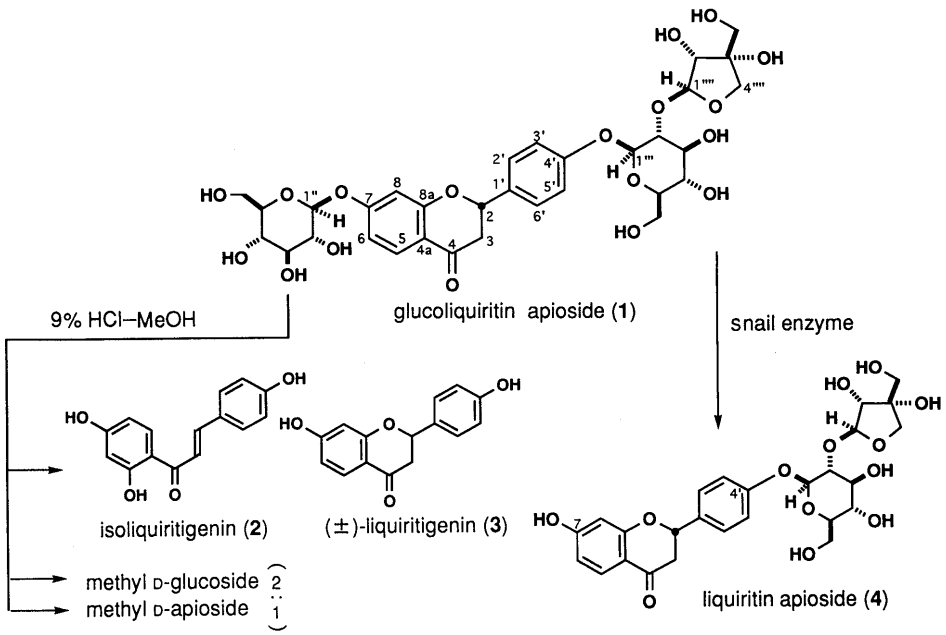



Fig. 2

TABLE I. $^{13}$C-NMR Data for Glucoliquiritin Apioside (**1**) and Liquiritin Apioside (**4**) (125 MHz, DMSO-$d_6$, $\delta_C$)

| | Carbons | 1 | 4 |
|---|---|---|---|
| Flavanone moiety | C-2 | 79.3 | 78.4 |
| | C-3 | 42.9 | 43.1 |
| | C-4 | 190.5 | 189.7 |
| | C-4a | 115.6 | 113.3 |
| | C-5 | 128.2 | 128.2 |
| | C-6 | 111.3 | 110.7 |
| | C-7 | 163.8 | 165.0 |
| | C-8 | 103.8 | 102.6 |
| | C-8a | 163.0 | 163.0 |
| | C-1′ | 131.7 | 132.4 |
| | C-2′,6′ | 128.3 | 127.9 |
| | C-3′,5′ | 116.4 | 116.1 |
| | C-4′ | 157.6 | 157.3 |
| 4′-*O*-β-D-Glucopyranosyl moiety | C-1‴ (or C-1″) | 99.1 | 98.8 |
| | C-2‴ (or C-2″) | 76.5[a] | 75.9[a] |
| | C-3‴ (or C-3″) | 76.6[a] | 76.1[a] |
| | C-4‴ (or C-4″) | 70.0[b] | 70.0 |
| | C-5‴ (or C-5″) | 77.1 | 77.0 |
| | C-6‴ (or C-6″) | 60.9 | 60.6 |
| β-D-Apiofuranosyl moiety | C-1⁗ (or C-1‴) | 109.0 | 108.7 |
| | C-2⁗ (or C-2‴) | 76.8[a] | 76.8 |
| | C-3⁗ (or C-3‴) | 79.5 | 79.2 |
| | C-4⁗ (or C-4‴) | 74.1 | 73.9 |
| | C-5⁗ (or C-5‴) | 64.5 | 64.3 |
| 7-*O*-β-D-Glucopyranosyl moiety | C-1″ | 100.1 | |
| | C-2″ | 73.3 | |
| | C-3″ | 76.6[a] | |
| | C-4″ | 70.2[b] | |
| | C-5″ | 76.9[a] | |
| | C-6″ | 74.1 | |

*a, b*) Assignments may be interchangeable within the same column.

d, $J$ = 1.6 Hz), and $\delta$ 7.22 (1H, dd, $J$ = 8.3, 1.6 Hz) suggested the presence of a 1,2,4-trisubstituted benzene ring in **7**.

Detailed comparison of the $^{13}$C-NMR data for shinflavanone (**7**) with those for glabrol (**8**) showed that **7** had the same B and C ring structures as those of **8**. Furthermore, from the $^{13}$C-NMR and $^{1}$H-NMR analyses of **7**, it was shown that **7** had a 6,6-dimethylpyran unit fused to the A ring, attached to the C-7 (through an oxygen) and C-8 positions. Thus, the *ortho*-coupled proton signals were observed at $\delta$ 6.49 (1H, d, $J$ = 8.6 Hz, 6-H), $\delta$ 7.74 (1H, d, $J$ = 8.6 Hz, 5-H), and a COLOC correlation was observed between the proton signal at $\delta$ 7.74 (5-H) and the carbon signals at $\delta_C$ 191.3 (C-4), 114.8 (C-4a), and 116.0 (C-6).

The absolute configuration at C-2 of **7** was demonstrated as *S* on the basis of the CD spectrum[19] of **7**, which showed a similar pattern, $[\theta]_{338}$ $+6.3\times10^3$ (positive maximum), $[\theta]_{302}$ $-6.1\times10^3$ (negative maximum), to that of glucoliquiritin apioside (**1**) (*vide supra*).

Consequently, the structure of shinflavanone (**7**) has been elucidated as 4′-hydroxy-3′-(3″,3″-dimethylallyl)-6‴,6‴-dimethylpyrano[2‴,3‴:7,8][2*S*]flavanone.

**Shinpterocarpin (9) and 1-Methoxyphaseollin (12)** Shinpterocarpin (**9**) was obtained as a yellowish oily compound. The molecular composition was defined as $C_{20}H_{18}O_4$ by the high-resolution EI-MS analysis. The $^{1}$H-NMR spectrum of **9** showed four one-proton signals at $\delta$ 3.65 (dd, $J$ = 9.4, 10.5 Hz) and $\delta$ 4.33 (dd, $J$ = 4.4, 10.5 Hz) due to 6-$H_2$, at $\delta$ 3.61 (m) due to 6a-H, and at $\delta$ 5.44 (d, $J$ = 6.6 Hz) due to 11a-H, which were reminiscent of a pterocarpan skeleton. A comparison of the $^{1}$H- and $^{13}$C-NMR data (Table III) for **9** with those for *ent*-(−)-hemileiocarpin (**10**)[15,16] and medicarpin (**11**),[14] led to the plane structure of **9** as shown in Fig 5. This was also supported by the observation of COLOC correlations between the proton signal at $\delta$ 7.25 (1-H) and the carbon signals at $\delta_C$ 110.7 (C-2), 151.3 (C-3), 116.7 (C-11b), and 78.8 (C-11a).

Shinpterocarpin (**9**) contains two chiral centers at C-6a and C-11a which were considered to possess either *R,R* or *S,S* configurations from the stereochemical environment around the C-6a and C-11a.[20] Moreover, it has been

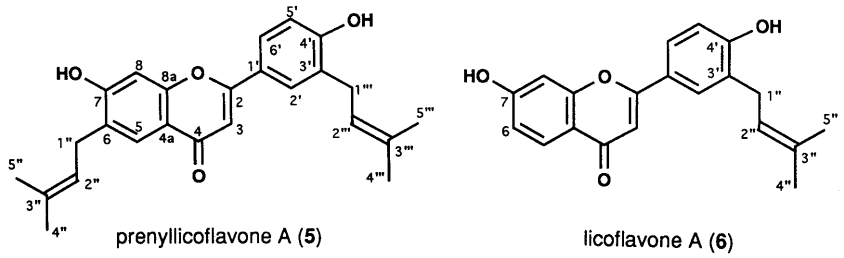



Fig. 3

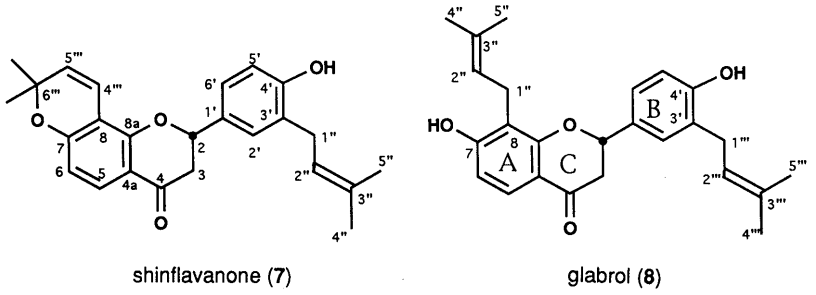



Fig. 4

TABLE II. $^{13}$C-NMR Data for Prenyllicoflavone A (**5**), Licoflavone A (**6**), Shinflavanone (**7**), and Glabrol (**8**) ($\delta_C$)

| | Carbons | **5**[a] | **6**[a] | **7**[b] | **8**[b] |
|---|---|---|---|---|---|
| Flavone (flavanone) moiety | C-2 | 162.7 | 161.3 | 79.8 | 79.5 |
| | C-3 | 105.4 | 105.8 | 44.2 | 44.0 |
| | C-4 | 177.8 | 177.4 | 191.3 | 192.6 |
| | C-4a | 117.3 | 117.3 | 114.8 | 114.8 |
| | C-5 | 126.1 | 126.1 | 125.1 | 126.6 |
| | C-6 | 128.5 | 128.4 | 116.0 | 115.8 |
| | C-7 | 164.0 | 163.5 | 150.8 | 161.8 |
| | C-8 | 102.8 | 102.9 | 109.5 | 115.0 |
| | C-8a | 157.1 | 161.1 | 159.8 | 161.2 |
| | C-1′ | 123.6 | 124.0 | 131.0 | 131.1 |
| | C-2′ | 126.2 | 128.8 | 128.1 | 128.0 |
| | C-3′ | 129.7 | 116.7 | 127.2 | 127.4 |
| | C-4′ | 159.2 | 161.7 | 154.8 | 154.7 |
| | C-5′ | 116.1 | 116.7 | 111.2 | 111.2 |
| | C-6′ | 128.5 | 128.8 | 125.6 | 125.4 |
| 6-Prenyl moiety | C-1″ | 28.6 | | | |
| | C-2″ | 122.7[c] | | | |
| | C-3″ | 133.1[d] | | | |
| | C-4″ | 25.9 | | | |
| | C-5″ | 17.9 | | | |
| 8-Prenyl moiety | C-1″ | | | | 22.3 |
| | C-2″ | | | | 121.5[c] |
| | C-3″ | | | | 134.6[d] |
| | C-4″ | | | | 25.9 |
| | C-5″ | | | | 18.0 |
| 3′-Prenyl moiety | C-1″ (or C-1‴) | 29.0 | 28.6 | 29.8 | 29.7 |
| | C-2″ (or C-2‴) | 123.1[c] | 122.7 | 121.4 | 121.3[c] |
| | C-3″ (or C-3‴) | 133.4[d] | 133.5 | 135.2 | 135.0[d] |
| | C-4″ (or C-4‴) | 25.9 | 25.9 | 25.9 | 25.9 |
| | C-5″ (or C-5‴) | 17.9 | 17.8 | 18.0 | 18.0 |
| 6‴,6‴-Dimethypyrano-[2‴,3‴:7,8]-moiety | C-4‴ | | | 116.0 | |
| | C-5‴ | | | 128.0 | |
| | C-6‴ | | | 77.0 | |
| | 6‴,6‴-Dimethyl | | | 28.2, 28.5 | |

*a*) Measured at 67.8 MHz in acetone-$d_6$. *b*) Measured at 67.8 MHz in $CDCl_3$. *c, d*) Assignments may be interchangeable within the same column.

TABLE III. $^{13}$C-NMR Data for Shinpterocarpin (**9**), *ent*-(−)-Hemileiocarpin (**10**), Medicarpin (**11**), 1-Methoxyphaseollin (**12**), and Phaseollin (**13**) (in $CDCl_3$, $\delta_C$)

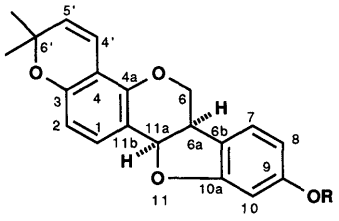
| Carbons | **9**[a] | **10**[a] | **11**[a] | **12**[a] | **13**[b] |
|---|---|---|---|---|---|
| C-1 | 129.3 | 129.2 | 132.3 | 158.1 | 132.3 |
| C-2 | 110.7 | 110.5 | 109.9 | 92.7 | 109.7 |
| C-3 | 151.3 | 151.2 | 157.3 | 161.3 | 157.1 |
| C-4 | 112.7 | 112.2 | 103.7 | 96.1 | 103.7 |
| C-4a | 157.0 | 157.1 | 156.7 | 157.4 | 156.8 |
| C-6 | 66.8 | 66.7 | 66.6 | 66.5 | 66.6 |
| C-6a | 39.5 | 39.5 | 39.6 | 39.0 | 39.7 |
| C-6b | 119.5 | 119.2 | 119.2 | 119.1 | 119.1 |
| C-7 | 125.0 | 124.7 | 124.8 | 123.7 | 123.8 |
| C-8 | 98.5 | 96.9 | 97.0 | 108.5 | 108.6 |
| C-9 | 161.2 | 161.1 | 161.2 | 155.4 | 155.4 |
| C-10 | 107.7 | 106.3 | 106.6 | 106.4 | 106.3 |
| C-10a | 160.7 | 161.1 | 160.7 | 153.7 | 153.8 |
| C-11a | 78.8 | 78.9 | 78.7 | 76.8 | 78.7 |
| C-11b | 116.7 | 116.5 | 112.5 | 101.5 | 112.7 |
| C-4′ | 116.6 | 116.5 | | 117.0 | 116.5 |
| C-5′ | 130.9 | 130.8 | | 129.3 | 130.4 |
| C-6′ | 76.3 | 76.1 | | 75.9 | 76.6 |
| 6′,6′-Dimethyl | 27.8, 29.8 | 27.9, 29.7 | | 27.9, 29.8 | 28.0, 28.0 |
| 9-$OCH_3$ | | 55.5 | 55.6 | | |
| 1-$OCH_3$ | | | | 60.2 | |

*a*) Measured at 67.8 MHz. *b*) Cited in reference 21*d*.

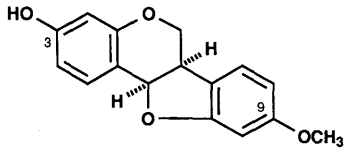
generally accepted that the absolute configuration of a pterocarpan compound may be presumed from the sign of the optical rotation.[20] That is, the levorotatory pterocarpans have 6a*R*, 11a*R* configurations, while the dextrorotatory ones have 6a*S*, 11a*S* configurations. In the case of shinpterocarpin (**9**), the value of the specific rotation of **9** was found to be −9.9°, so that the absolute configuration of **9** was presumed to be 6a*R*, and 11a*R*. In order to verify this presumption, compound **9** was methylated with diazomethane to afford the monomethyl ether, which was shown to be identical with *ent*-(−)-hemileiocarpin (**10**), isolated above by us.

Consequently, the chemical structure of shinpterocarpin is 9-hydroxy-6′,6′-dimethylpyrano[2′,3′:3,4][6a*R*,11a*R*]-pterocarpan (**9**).

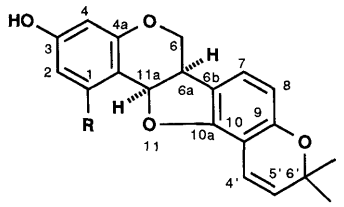
Another pterocarpan compound, 1-methoxyphaseollin (**12**), was obtained as a yellowish oily substance and the




shinpterocarpin (**9**) : R = H
*ent*-(-)-hemileiocarpin (**10**) : R = $CH_3$




medicarpin (**11**)




1-methoxyphaseollin (**12**) : R = $OCH_3$
phaseollin (**13**) : R = H

Fig. 5

molecular composition was defined as $C_{21}H_{20}O_5$ from the high-resolution EI-MS analysis. The presence of a free phenolic hydroxyl group in **12** was shown by a positive ferric chloride test. Detailed comparison of the $^1$H-NMR and $^{13}$C-NMR data (Table III) for **12** with those for medicarpin (**11**)[14] and phaseollin (**13**)[21] led us to presume that **12** had a pterocarpan skeleton with a fused dimethylpyran ring. Furthermore, the nuclear Overhauser effect (NOE) was observed between the methoxyl protons ($\delta$ 3.85) and two protons at C-11a ($\delta$ 5.60, d, $J$=6.4 Hz, 7.1%) and C-2 ($\delta$ 6.02, d, $J$=1.9 Hz, 8.5%), which supported the location of the methoxyl group of **12** at C-1. Here again, the value of the specific rotation of **12** ($[\alpha]_D$ −16.7°) indicated the absolute configuration to be the same (6a*R*, 11a*R*) as that of shinpterocarpin (**9**).

From the above-mentioned evidence, the structure of 1-methoxyphaseollin has been determined as 1-methoxy-3-hydroxy-6′,6′-dimethylpyrano[2′,3′:9,10][6a*R*,11a*R*]-pterocarpan (**12**).

In conclusion, we have isolated five new flavonoid constituents from roots of *Glycyrrhiza glabra* L. from the Xinjiang area, China. Among these five constituents, only prenyllicoflavone A (**5**) has been isolated from the roots of *Glycyrrhiza inflata* BATALIN, another Xinjiang licorice. With various constituents such as flavonoids, saponins, *etc.* at hand, we are currently engaged in comparative analyses of flavonoid and saponin constituents in various Chinese licorice roots of different origins, which will be reported in our forthcoming paper.

**Experimental**

Melting points were determined on a Yanagimoto micro-melting point apparatus and recorded as read. The UV spectra were obtained with a Hitachi 330 spectrophotometer, whereas the IR spectra were measured with a Hitachi 260-30 (by a KBr disk or a $CHCl_3$ solution transmittance method) or JASCO FTIR-5300 (by a diffusion reflection method on KBr powder) spectrometer. The optical rotations were measured with a JASCO DIP-370 digital polarimeter in a 0.5 dm length cell, while the CD spectra were recorded on a JASCO J-500A spectropolarimeter equipped with a 501N data processor. The EI-MS were taken on a JEOL JMS-D300 spectrometer, whereas the FAB-MS were taken on a JEOL SX102 spectrometer. The $^1$H- and $^{13}$C-NMR spectra were measured with a JEOL JNM GX-500 or EX-270 spectrometer. For GLC and HPLC, a Shimadzu GC-9A gas chromatograph and a Shimadzu LC-6A HPLC system were used. Column chromatography (ordinary-phase) was carried out using Kieselgel 60 (70—230 mesh, Merck). Thin-layer chromatography (TLC) was conducted on precoated Kieselgel 60$F_{254}$ plates (0.2 mm thickness, Merck). Spots were detected by spraying 1% $Ce(SO_4)_2$/10% $H_2SO_4$ aqueous solution on the TLC plates, followed by heating.

**Isolation of Fifteen Flavonoids, Eight Saponins, and Eight Flavonoid Glycosides** The air-dried roots of *Glycyrrhiza glabra* L. (from Xinjiang province, China, cut, 0.9 kg) were extracted three times with MeOH (3 l each) under reflux. Evaporation of the solvent under reduced pressure from the combined extract gave the MeOH extract (155 g). The extract (100 g) was then partitioned into an ethyl acetate–water (1 : 1) mixture (1.5 l). Removal of the solvent from the water phase and the ethyl acetate phase under reduced pressure below 40 °C yielded the aqueous extract (67 g) and the ethyl acetate extract (33 g). The ethyl acetate extract (30 g) was subjected to silica gel column chromatography [silica gel 700 g, gradient elution with *n*-hexane–ethyl acetate (7 : 1→0 : 1)] to furnish five fractions: fraction 1 (fr. 1) [eluted with *n*-hexane–ethyl acetate (7 : 1→5 : 1), 2.2 g], fraction 2 (fr. 2) [eluted with *n*-hexane–ethyl acetate (5 : 1→3 : 1), 3.4 g], fraction 3 (fr. 3) [eluted with *n*-hexane–ethyl acetate (3 : 1), 7.7 g], fraction 4 (fr. 4) [eluted with *n*-hexane–ethyl acetate (2 : 1→1 : 1), 1.8 g], and later eluates [eluted with ethyl acetate, 3.8 g]. Silica gel column chromatography [$SiO_2$ 50 g, $CHCl_3$–MeOH (40 : 1)] of fr. 1 (1.8 g) afforded a flavonoid mixture together with licoflavone A, prenyllicochalcone A (**5**) and echinatin in 0.18, 0.10, and 0.03% yields from the air-dried roots, respectively. The flavonoid mixture was further purified by semi-preparative HPLC [Zorbax SIL, 8 mm × 25 cm, *n*-hexane–ethyl acetate (7 : 1)] to provide *ent*-(−)-hemileiocarpin (**10**), hispaglabridin A, and methylhispaglabridin B in 0.001, 0.007, and 0.0006% yields from the air-dried roots, respectively. Silica gel column chromatography [$SiO_2$ 100 g, $CHCl_3$–MeOH (20 : 1)] of fr. 2 (3.0 g) followed by semi-preparative HPLC [Zorbax SIL, 8 mm × 25 cm, *n*-hexane–acetone (7 : 1)] afforded hispaglabridin B, shinflavanone (**7**), glabrene, and shinpterocarpin (**9**) in 0.007, 0.002, 0.05, and 0.001% yields from the roots, respectively. Silica gel column chromatography [$SiO_2$ 150 g, *n*-hexane–ethyl acetate (5 : 1)] of fr. 3 (7.0 g) followed by Lobar column chromatography [size B SIL, *n*-hexane–acetone (3 : 1)] afforded medicarpin (**11**), licochalcone B, glabrol (**8**), and licoflavone A (**6**) in 0.09, 0.01, 0.13, and 0.10% yields from the roots, respectively. Finally, silica gel column chromatography [$SiO_2$ 30 g, $CHCl_3$–MeOH (40 : 1)] of fr. 4 (1.5 g) followed by semi-preparative HPLC [Zorbax SIL, 8 mm × 25 cm, $CHCl_3$–EtOH (20 : 1)], provided 1-methoxyphaseollin (**12**) in 0.007% yield from the roots. Next, a part of the aqueous extract (45 g) was subjected to reversed-phase silica gel column chromatography [Fuji-gel RQ-3 250 g, with gradient elution: $H_2O$–MeOH (9 : 1→1 : 9)] to furnish three fractions: fr. A [eluted with $H_2O$–MeOH (9:1→6:1), mainly sugars, 13 g], fr. B [eluted with $H_2O$–MeOH (6 : 1→4 : 1), mainly sugars and flavonoid glycosides, 12 g] and fr. C [eluted with $H_2O$–MeOH (4 : 1→3 : 1), mainly saponins, 7.7 g), and later eluates combined [eluted with $H_2O$–MeOH (2 : 1→1 : 9), 10 g]. Silica gel column chromatography [$SiO_2$ 300 g, gradient elution with $CHCl_3$–MeOH–$H_2O$ (10 : 3 : 1 lower phase→5 : 3 : 1)] of fr. B (10 g) and subsequent preparative HPLC separation [Shim-pack PREP-ODS, 30 mm × 25 cm, MeOH–$H_2O$ (5 : 1)] provided ononin, liquiritin, liquiritin apioside (**4**), isoliquiritin, neoisoliquiritin, licuraside, isoliquiritin apioside, and glucoliquiritin apioside (**1**), in 0.07, 0.24, 0.98, 0.15, 0.03, 0.20, 1.65, and 0.004% yields from the roots, respectively. Silica gel column chromatography [gradient elution with $CHCl_3$–MeOH–$H_2O$ (6 : 4 : 1→5 : 5 : 1)] followed by semi-preparative HPLC [YMC AM-323 (ODS), $CH_3CN$–1% aqueous AcOH (65 : 35)] of fr. C provided glycyrrhizin, licorice-saponins A3, C2, E2, G2, H2, apioglycyrrhizin, and araboglycyrrhizin in 1.56, 0.04, 0.006, 0.08, 0.09, 0.23, 0.02, and 0.02% yields from the roots, respectively.

Glucoliquiritin Apioside (**1**): mp 157—158 °C (pale yellow fine crystals from $CHCl_3$–MeOH–$H_2O$), $[\alpha]_D$ −80° ($c$=0.35, MeOH, 20 °C). High-resolution FAB-MS (positive) $m/z$: Found: 735.2075; Calcd for $C_{32}H_{40}NaO_{18}$ [$(M+Na)^+$]: 735.2111. UV (MeOH) $\lambda_{max}$ nm ($\varepsilon$): 269 (4000), 314 (1700); (+NaOMe or +NaOAc): 269, 313. CD (MeOH,

$c=1.3\times10^{-3}$, 20 °C) : $[\theta]_{330}$ $+9.7\times10^3$ (pos. max.), $[\theta]_{315}$ 0, $[\theta]_{287}$ $-1.1\times10^4$ (neg. max.). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3600—3000 (br), 1664, 1514, 1444, 1254, 1076. $^1$H-NMR (500 MHz, DMSO-$d_6$) $\delta$: 2.74 (1H, dd, $J=16.2$, 3.0 Hz, 3$\beta$-H), 3.16—3.52 (15H, m, sugar protons and 3$\alpha$-H), 3.64 (1H, d, $J=9.2$ Hz, 4''''$\beta$-H), 3.69 (1H, br s, $W_{1/2}=ca.$ 6 Hz, 2''''-H), 3.94 (1H, d, $J=9.2$ Hz, 4''''$\alpha$-H), 4.92 (1H, d, $J=7.3$ Hz, 1''-H), 4.97 (1H, d, $J=7.0$ Hz, 1'''-H), 5.36 (1H, br s, $W_{1/2}=ca.$ 6 Hz, 1''''-H), 5.66 (1H, dd, $J=3.0$, 13.2 Hz, 2-H), 6.68 (1H, d, $J=2.1$ Hz, 8-H), 6.72 (1H, dd, $J=2.1$, 8.8 Hz, 6-H), 7.05 (2H, d, $J=8.5$ Hz, 3'-H, 5'-H), 7.45 (2H, d, $J=8.5$ Hz, 2'-H, 6'-H), 7.72 (1H, d, $J=8.8$ Hz, 5-H). $^{13}$C-NMR: as given in Table I. FAB-MS (positive) $m/z$: 735 $(M+Na)^+$, 345, 329, 257.

Prenyllicoflavone A (**5**): A yellowish oil. High-resolution EI-MS $m/z$: Found: 390.1807; Calcd for $C_{25}H_{26}O_4$ ($M^+$): 390.1828. UV $\lambda_{max}^{MeOH}$ nm ($\varepsilon$): 233 (31800), 254 sh, 335 (30100); (+$AlCl_3$): 264, 336; (+NaOMe): 267, 340, 405. IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3375—3180 (br), 1624, 1567, 1367, 1250. $^1$H-NMR (500 MHz, acetone-$d_6$) $\delta$: 1.74 (3H, s), 1.76 (9H, s) (totally four prenylmethyls), 3.41 (4H, d, $J=7.3$ Hz, 1''-$H_2$, 1'''-$H_2$), 5.40, 5.41 (both 1H, d, $J=7.3$ Hz, 2''-H, 2'''-H), 6.59 (1H, s, 3-H), 7.01 (1H, d, $J=8.6$ Hz, 5'-H), 7.04 (1H, s, 8-H), 7.72 (1H, dd, $J=2.1$, 8.6 Hz, 6'-H), 7.78 (1H, d, $J=2.1$ Hz, 2'-H), 7.82 (1H, s, 5-H). $^{13}$C-NMR: as given in Table II. EI-MS $m/z$ (%): 390 ($M^+$, 100), 376 [$(M-CH_3)^+$, 67], 335 [$(M-C_4H_7)^+$, 85].

Shinflavanone (**7**): A yellowish oil, $[\alpha]_D$ $-14.7°$ ($c=0.53$, $CHCl_3$, 25 °C). High-resolution EI-MS $m/z$: Found: 390.1846; Calcd for $C_{25}H_{26}O_4$: 390.1828. UV $\lambda_{max}^{MeOH}$ nm ($\varepsilon$): 238 (18100), 275 (11000), 312 (8100); (+NaOMe or +NaOAc): 273, 320, 448; (+$AlCl_3$): 267, 312. CD (MeOH, $c=6.0\times10^{-3}$, 20 °C): $[\theta]_{338}$ $+6.3\times10^3$ (pos. max.), $[\theta]_{317}$ 0, $[\theta]_{302}$ $-6.1\times10^3$ (neg. max.). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3500—3200 (br), 1700, 1607, 1495, 1467, 1377. $^1$H-NMR (500 MHz, $CDCl_3$) $\delta$: 1.70, 1.71 (each 3H, s, 4'' and 5''-$H_3$), 1.44, 1.47 (each 3H, s, 6'''-$CH_3\times2$), 2.80 (1H, dd, $J=3.0$, 16.6 Hz, 3$\alpha$-H), 3.01 (1H, dd, $J=13.2$, 16.6 Hz, 3$\beta$-H), 3.39 (2H, d, $J=7.0$ Hz, 1''-$H_2$), 5.38 (1H, dd, $J=3.0$, 13.2 Hz, 2-H), 5.38 (1H, t, $J=7.0$ Hz, 2''-H), 5.56 (1H, d, $J=10.0$ Hz, 5'''-H), 6.49 (1H, d, $J=8.6$ Hz, 6-H), 6.63 (1H, d, $J=10.0$ Hz, 4'''-H), 6.85 (1H, d, $J=8.3$ Hz, 5'-H), 7.20 (1H, d, $J=1.6$ Hz, 2'-H), 7.22 (1H, dd, $J=8.3$, 1.6 Hz, 6'-H), 7.74 (1H, d, $J=8.6$ Hz, 5-H). $^{13}$C-NMR: as given in Table II. EI-MS $m/z$ (%): 390 ($M^+$, 22), 375 [$(M-CH_3)^+$, 33], 203 (20), 188 (18), 187 (100), 173 (22).

Shinpterocarpin (**9**): A yellowish oil, $[\alpha]_D$ $-9.9°$ ($c=1.02$, MeOH, 25 °C). High-resolution EI-MS $m/z$: Found: 322.1207; Calcd for $C_{20}H_{18}O_4$: 322.1208. UV $\lambda_{max}^{MeOH}$ nm ($\varepsilon$): 230 (24000), 281 (8100). CD (MeOH, $c=1.0\times10^{-3}$, 20 °C): $[\theta]_{291}$ $+1.9\times10^3$ (pos. max.), $[\theta]_{246}$ 0, $[\theta]_{236}$ $-5.3\times10^4$ (neg. max.). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3500—3300 (br), 1660, 1635, 1593, 1508, 1477, 1439, 1393, 1377. $^1$H-NMR (500 MHz, $CDCl_3$) $\delta$: 1.39 (6H, s, 6'-$CH_3\times2$), 3.61 (1H, m, 6a-H), 3.65 (1H, dd, $J=9.4$, 10.5 Hz, 6$\beta$-H), 4.33 (1H, dd, $J=4.4$, 10.5 Hz, 6$\alpha$-H), 5.48 (1H, d, $J=6.6$ Hz, 11a-H), 5.67 (1H, d, $J=9.9$ Hz, 5'-H), 6.31 (1H, d, $J=2.2$ Hz, 10-H), 6.38 (1H, dd, $J=2.2$, 8.3 Hz, 8-H), 6.48 (1H, d, $J=8.8$ Hz, 2-H), 6.60 (1H, d, $J=9.9$ Hz, 4'- H), 7.13 (1H, d, $J=8.3$ Hz, 7-H), 7.25 (1H, d, $J=8.8$ Hz, 1-H). $^{13}$C-NMR: as given in Table III. EI-MS $m/z$ (%): 322 ($M^+$, 46), 307 [$(M-CH_3)^+$, 100].

1-Methoxyphaseollin (**12**): A yellowish oil, $[\alpha]_D$ $-16.7°$ ($c=0.91$, MeOH, 25 °C). High-resolution EI-MS $m/z$: Found: 352.1311; Calcd for $C_{21}H_{20}O_5$: 352.1312. UV $\lambda_{max}^{MeOH}$ nm ($\varepsilon$): 224 (37000), 281 (12400). CD (MeOH, $c=1.0\times10^{-3}$, 20 °C): $[\theta]_{318}$ $+2.4\times10^3$ (pos. max.), $[\theta]_{249}$ 0, $[\theta]_{232}$ $-2.7\times10^4$ (neg. max.). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3400—3300 (br), 1593, 1452, 1363, 1342, 1308. $^1$H-NMR (500 MHz, $CDCl_3$) $\delta$: 1.39, 1.41 (each 3H, s, 6'-$CH_3\times2$), 3.34 (1H, m, 6a-H), 3.59 (1H, dd, $J=11.1$, 11.1 Hz, 6$\beta$-H), 3.85 (3H, s, 1-$OCH_3$), 4.17 (1H, dd, $J=5.1$, 11.1 Hz, 6$\alpha$-H), 5.54 (1H, d, $J=9.8$ Hz, 5'-H), 5.60 (1H, d, $J=6.4$ Hz, 11a-H), 6.02 (1H, d, $J=1.9$ Hz, 2-H), 6.08 (1H, d, $J=1.9$ Hz, 4-H), 6.33 (1H, d, $J=8.1$ Hz, 8-H), 6.55 (1H, d, $J=9.8$ Hz, 4'-H), 6.92 (1H, d, $J=8.1$ Hz, 7-H). $^{13}$C-NMR: as given in Table III. EI-MS $m/z$ (%): 352 ($M^+$, 55), 337 [$(M-CH_3)^+$, 100], 309 [$(M-CH_3-H_2O)^+$, 16].

**Methanolysis of Glucoliquiritin Apioside (1)** A solution of **1** (20 mg) in 9% HCl–MeOH (2 ml) was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with an $Ag_2CO_3$ powder and the whole was filtered to remove the inorganic material. After removal of the solvent from the filtrate under reduced pressure, the product (19 mg) was purified by silica gel column chromatography [$SiO_2$ 8 g, $CHCl_3$–MeOH (20:1→3:2)] to give isoliquiritigenin (**2**, 2.8 mg), (±)-liquiritigenin (**3**, 3.0 mg), and a methyl glycoside fraction (7.6 mg). Silylation of the methyl glycoside fraction (0.6 mg) with TMS-HT solution (Tokyo Kasei Industries, hexamethyldisilazane and trimethylchlorosilane in pyridine, 0.5 ml) gave the trimethylsilyl derivatives of methyl D-glucoside and methyl D-apioside, which were identified by GLC comparison with respective authentic samples. GLC analysis: 3% SE-30 on Uniport B (80—100 mesh); 3 mm (i.d.) × 1 m, glass column, column temperature 140 °C; $N_2$ flow rate 40 ml/min; $t_R$ TMS derivatives of methyl apioside 8 min 25 s and 9 min 3 s; TMS derivatives of methyl glucoside 32 min 24 s and 36 min 54 s. The area ratio of TMS derivatives of methyl apioside and methyl glucoside on GLC was 1:2. Isoliquiritigenin (**2**) and liquiritigenin (**3**) were identified by comparisons of the IR, UV, and $^1$H-NMR data with those of authentic samples, and by mixed melting point determination, respectively. The methyl glycoside fraction (5 mg) was subjected to silica gel column chromatography [$SiO_2$, 1.5 g, $CHCl_3$–MeOH (10:1)] to afford methyl D-apioside (1.4 mg) and methyl D-glucoside (2.6 mg). Methyl D-apioside obtained from **1** was dissolved in 5% aqueous $H_2SO_4$ (0.5 ml) and the mixture was heated under reflux for 2 h. The reaction mixture was neutralized with Dowex 1 × 2 ($OH^-$ form) and the resin was removed by filtration. Evaporation of the solvent from the filtrate under reduced pressure provided D-apiose $[\alpha]_D$ $+8°$ ($c=0.07$, $H_2O$, 20 °C, in a quartz cell, measured 24 h later after dissolving in $H_2O$). A solution of methyl D-glucoside (2.4 mg) obtained from **1** was dissolved in 5% aqueous $H_2SO_4$ (0.5 ml) and the mixture was heated under reflux for 2 h. The reaction mixture was worked up as described above to afford D-glucose ($[\alpha]_D$ $+48°$, $c=0.18$, $H_2O$, 22 °C, measured 24 h later after dissolving in $H_2O$).

**Partial Hydrolysis of Glucoliquiritin Apioside (1) with Snail Enzyme** A solution of **1** (2 mg) in water (0.5 ml) was treated with snail enzyme[18] and the whole was incubated with gentle stirring at 37 °C for 2 d. After addition of *n*-BuOH (5 ml) and water (5 ml), the whole mixture was heated in a boiling water bath for 2 min. The whole was taken in a separatory funnel and the *n*-BuOH phase was separated. The aqueous phase was extracted with *n*-BuOH twice (3 ml each) and the combined *n*-BuOH phase was evaporated to dryness under reduced pressure. Preparative TLC [TLC plate: Merck #5744, Pre-Coated Silica gel $60GF_{254}$, 0.5 mm thickness, developed with $CHCl_3$–MeOH–$H_2O$ (6:4:1)] of the *n*-BuOH extract furnished isoliquiritin apioside (**4**, 1.0 mg), which was identical with the authentic sample[1] on the basis of TLC co-chromatography [1) $SiO_2$ plate developed with $CHCl_3$–MeOH–$H_2O$ (6:4:1), 2) reversed-phase $SiO_2$ plate Merck RP-18 developed with MeOH–$H_2O$ (2:3)] and IR (KBr) and $^1$H-NMR ($CD_3OD$) comparisons.

**Diazomethane Treatment of Shinpterocarpin (9) Giving *ent*-(−)-Hemileiocarpin (10)** An ice-cooled solution of **9** (3 mg) in diethyl ether (1 ml) was treated with ethereal diazomethane (*ca.* 5 ml) until the yellow color persisted. The solution was left standing for 5 h, then the solvent was removed under reduced pressure to furnish **10** (3 mg). **10** thus obtained was identified by comparison of optical rotation,[15] CD,[15] IR, and $^1$H-NMR data with those of the authentic sample isolated by us above.

## References and Notes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