Chemical Constituents from Fruits of *Gymnocladus chinensis*

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Abstract: **Objective** To study chemical constituents from fruits of *Gymnocladus chinensis*. **Methods** The compounds were isolated by various chromatographic techniques and their structures were elucidated on the basis of spectral analyses. **Results** Ten compounds were isolated from the EtOAc extract and were identified as 2-methyl pentyl (2*E*, 6*S*)-6-hydroxy-2, 6-dimethyl-2, 7-octadienoate (**1**), (2*E*, 6*S*)-6-α-L-arabino pyranosyloxy-2, 6-dimethyl-2, 7-octadienoic acid (**2**), ethyl (2*E*, 6*S*)-6-hydroxy-2, 6-dimethyl-2, 7-octadienoate (**3**), 5, 2′, 5′-trihydroxy-3, 7, 4′-trimethoxyflavone (**4**), (2*R*, 3*R*)-3, 3′, 5, 5′, 7-pentahydroxyflavanone (**5**), 2′, 4′-dihydroxy-4-methoxychalcone (**6**), kaempferol (**7**), apigenin (**8**), 4′, 7-dihydroxyflavone (**9**), and 5, 7, 4′-trihydroxy-3′-methoxyflavone (**10**). **Conclusion** Compound **1** is a new compound, compound **3** is firstly obtained from natural source, and compounds **4** – **10** are isolated from *G. chinensis* for the first time. Furthermore, the assignments of ^{13}C-NMR data of compounds **3** and **4** are reported in this paper for the first time.

Key words: chemical constituents; flavone; *Gymnocladus chinensis* Baill.; monoterpene
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Introduction

Gymnocladus chinensis Baill. (Leguminosae) is a tall tree, widely distributed in South China. The dried fruits of this plant are used as a crude drug *Feizaojia* in Chinese materia medica as diuretics and expectorants (Editorial Office of National Chinese Herb Medicine Collection, 1996). Previous phytochemical studies showed ten saponins (Konoshima *et al*, 1984, Konoshima *et al*, 1985, Konoshima *et al*, 1987, Konoshima *et al*, 1995, Ma *et al*, 2007), two monoterpene glycosides (Konoshima and Sawada, 1984), and one peptide (Wong and Ng, 2003) were obtained from the fruits of this plant. Some of saponins from *G. chinensis* showed anti-HIV and anticancer effects (Konoshima *et al*, 1995, Ma *et al*, 2007). As to search for novel bioactive constituents from natural source, we investigated the chemical constituents of *G. chinensis*. In the present paper, we described the isolation and structure elucidation of one new monoterpene derivative, as well as nine known compounds. Furthermore, the ^{13}C-NMR data of compounds **3** and **4** were assigned in this paper for the first time.

Materials and Methods

Experimental and plant material

Optical rotation was obtained on Perkin-Elmer 243B polarimeter. IR spectra were recorded on Thermo Nicolet Nexus 470 FT-IR spectrometer. NMR spectra were measured on Bruker advance DRX 500 spectrometer. ESI-MS was taken by triple quadrupole mass spectrometer (Quattro VG Biotech and Finnigan MAT 311A). FAB-MS were measured on Bruker Daltonics, APEX II FT-ICR mass spectrometer. Silica gel (100–200 meshes and 200–300 meshes) for column chromatography and GF_{254} silica gel for TLC were collected by Qingdao

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Marine Chemistry Co. Sephadex LH-20 column chromatography was obtained from Amersham Bio-sciences Co., Shanghai, China.

Samples of the fruits of *G. chinensis* were collected in Mianyang, Sichuan Province, China, in October, 2002 and were authenticated by Prof. SUN Qishi, Shenyang Pharmaceutical University, China. A specimen of the plant was deposited at State Key Laboratory of Natural and Biomimetic Drugs, Peking University, Beijing, China (GC-FZJ0210). The fruits were air-dried and milled.

Extraction and isolation

The pulverized plant material (4 kg) was extracted with 95% hot ethanol (16 L) three times, 2 h each time. The combined ethanol extracts were evaporated under reduced pressure. A suspension of this crude extract in distilled water was extracted with petroleum ether, EtOAc, and *n*-BuOH, respectively to yield about 15.6 g of a petroleum ether extract, 32.0 g of an EtOAc extract, 122.2 g of a dried *n*-BuOH extract, and an aqueous residue. The EtOAc extract was subjected to silica gel column chromatography, eluted with $CHCl_3$-MeOH (50 : 1–1 : 1). The eluents were combined to afford eight fractions (Fr. A–Fr. H) on the basis of TLC analysis. Fraction A (9.2 g) was further fractionated into six sub-fractions (A_1 – A_6) according to TLC by using silica gel column chromatography. Sub-fraction A_2 (520 mg) was subjected to silica gel column chromatography (petroleum ether–EtOAc = 5 : 1) to yield compounds **1** (7.8 mg) and **3** (12.8 mg). Sub-fraction A_3 (484 mg) was subjected to Sephadex LH-20 column chromatography (CH_3OH), then further separated by silica gel column chromatography ($CHCl_3$–MeOH = 18 : 1) to afford compounds **4** (18.5 mg), **8** (12.3 mg), and **10** (23.0 mg). Sub-fraction A_4 (1.24 g) was subjected to repetitive silica gel column chromatography ($CHCl_3$ – MeOH = 15 : 1) to afford compounds **6** (32.8 mg), **7** (15.9 mg), and **9** (25.0 mg). Sub-fraction A_5 (2.20 g) was separated by silica gel column chromatography (petroleum ether–EtOAc = 1 : 1) to afford four fractions, Fr. $A_{5\text{-}3}$ (347 mg) was subjected to Sephadex LH-20 column chromatography (CH_3OH) to afford compound **5** (26.0 mg). Fraction E was recrystallized from MeOH to give compound **2** (36.2 mg).

Results

Compound 1: colorless oil; $[\alpha]_D^{25}$ + 8.7° (*c* 0.31, MeOH); IR (KBr) ν_{max} 3 480, 2 964, 2 931, 1 710, 1 647, 1 462, 1 276, 1 160, 1 104, 1 076, 996, 921 cm^{-1}; ESI–MS *m/z*: 269 $[M + H]^+$, 291 $[M + Na]^{+1}$, ^1H and ^{13}C-NMR, see Table 1.

Compound **2**: white amorphous solid; $[\alpha]_D^{27}$ + 4.7° (*c* 1.07, MeOH); FAB–MS *m/z*: 317 $[M + H]^+$, 298 $[M – H_2O]^+$, 280 $[M – 2H_2O]^+$, 184 $[M + H – 133]^+$, 167 [M – Arab]$^+$, 149 $[M – 167]^+$, 133 $[M + H – 184]^+$; ^1H and ^{13}C-NMR, see Table 1. These data were consistent with those of reference (Konoshima and Sawada, 1984).

Compound **3**: colorless oil; $[\alpha]_D^{25}$ + 15.8° (*c* 0.53, $CHCl_3$); ESI–MS *m/z*: 213 $[M + H]^+$, 230 $[M + NH_4]^+$; ^1H and ^{13}C-NMR, see Table 1. These data were consistent with those of reference (Carda *et al*, 1995).

Compound **4**: yellow amorphous powder; ^1H-NMR (500 MHz, DMSO-d_6) δ: 12.70 (1H, s, OH-5), 9.31 (1H, s, OH-2′), 8.63 (1H, s, OH-5′), 6.77 (1H, s, H-6′), 6.59 (1H, d, *J* = 2.2 Hz, H-8), 6.53 (1H, s, H-3′), 6.37 (1H, d, *J* = 2.2 Hz, H-6), 3.83 (3H, s, OMe-7), 3.78 (3H, s, OMe-4′), 3.70 (3H, s, OMe-3); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 179.1 (C-4), 165.9 (C-7), 161.9 (C-5), 158.2 (C-2), 157.8 (C-9), 151.6 (C-4′), 149.9 (C-2′), 139.9 (C-3), 139.7 (C-5′), 116.8 (C-6′), 109.0 (C-1′), 106.5 (C-10), 101.8 (C-3′), 98.6 (C-6), 93.1 (C-8), 60.8 (3-OMe), 56.9 (7-OMe), 56.3 (4′-OMe). The ^1H-NMR data were consistent with those of reference (Braz and Gottlieb, 1971).

Compound **5**: light yellow amorphous powder; $[\alpha]_D^{25}$ + 23.8° (*c* 1.2, CH_3OH); ^1H-NMR (500 MHz, DMSO-d_6) δ: 11.89 (1H, s, OH-5), 10.81 (1H, s, OH-7), 9.02 (1H, s, OH), 8.97 (1H, s, OH), 6.86 (1H, brs, H-4′), 6.73 (2H, brs, H-2′, H-6′), 5.89 (1H, d, *J* = 2.0 Hz, H-6), 5.84 (1H, d, *J* = 2.0 Hz, H-8), 5.75 (1H, d, *J* = 6.2 Hz, OH-3), 4.96 (1H, d, *J* = 10.7 Hz, H-2), 4.49 (1H, dd, *J* = 10.7, 6.2 Hz, H-3); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 198.1 (C-4), 167.1 (C-7), 163.7 (C-5), 162.9 (C-9),

146.1 (C-3′), 145.3 (C-5′), 128.4 (C-1′), 119.7 (C-4′), 115.7 (C-2′), 115.5 (C-6′), 100.8 (C-10), 96.3 (C-6), 95.3 (C-8), 83.4 (C-2), 71.9 (C-3). These data were consistent with those of reference (Ding *et al*, 1997).

Compound **6**: yellow amorphous powder; ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 10.25(1H, s, OH), 9.99 (1H, s, OH), 7.55 (2H, d, J = 8.5 Hz, H-2, H-6), 7.52 (1H, d, J = 8.5 Hz, H-6′), 7.47 (1H, d, J = 15.7 Hz, H-β), 7.37 (1H, d, J = 15.7 Hz, H-α), 6.82 (2H, d, J = 8.5 Hz, H-3, H-5), 6.51 (1H, d, J = 2.1 Hz, H-3′), 6.46 (1H, dd, J = 8.5, 2.1 Hz, H-5′), 3.85 (3H, s, 4-OMe); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 189.7 (-CO-), 163.4 (C-4), 161.3 (C-2′), 160.5 (C-4′), 142.2 (C-β), 133.1 (C-6′), 131.1 (C-2, 6), 126.9 (C-1), 124.8 (C-α), 121.1 (C-1′), 116.7 (C-3, 5), 108.7 (C-5′), 100.1 (C-3′). These data were consistent with those of reference (Achenbach *et al*, 1988).

Compound **7**: yellow amorphous powder; ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 12.48 (1H, s, OH-5), 10.82 (1H, s, OH-7), 10.13 (1H, s, OH), 9.41 (1H, s, OH), 8.05 (2H, d, J = 8.9 Hz, H-2′, H-6′), 6.93 (2H, d, J = 8.9 Hz, H-3′, H-5′), 6.45 (1H, d, J = 2.1 Hz, H-8), 6.19 (1H, d, J = 2.1 Hz, H-6); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 176.8 (C-4), 164.8 (C-7), 161.6 (C-5), 160.1 (C-4′), 157.0 (C-9), 147.7 (C-2), 136.5 (C-3), 130.4 (C-2′, C-6′), 122.5 (C-1′), 116.3 (C-3′, C-5′), 103.9 (C-10), 99.1 (C-6), 94.3 (C-8). These data were consistent with those of reference (Yu and Yang, 1999).

Compound **8**: yellow amorphous powder; ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 12.97 (1H, s, OH-5), 10.83 (1H, s, OH), 10.35 (1H, s, OH), 7.93 (2H, d, J = 8.7 Hz, H-2′, H-6′), 6.94 (2H, d, J = 8.7 Hz, H-3′, H-5′), 6.79 (1H, s, H-3), 6.51 (1H, d, J = 2.1 Hz, H-8), 6.21 (1H, d, J = 2.1 Hz, H-6); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 182.6 (C-4), 165.1 (C-2), 164.6 (C-7), 162.3 (C-4′), 162.0 (C-5), 158.1 (C-9), 129.3 (C-2′, C-6′), 122.0 (C-1′), 116.8 (C-3′, C-5′), 104.5 (C-10), 103.6 (C-3), 99.7 (C-6), 94.8 (C-8). These data were consistent with those of reference (Yu and Yang, 1999).

Compound **9**: yellow amorphous powder; ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 10.74 (1H, s, OH), 10.23 (1H, s, OH), 7.89 (2H, d, J = 8.7 Hz, H-2′, H-6′), 7.84 (1H, d, J = 8.5 Hz, H-5), 6.95 (1H, d, J = 2.1 Hz, H-8), 6.91 (2H, d, J = 8.7 Hz, H-3′, H-5′), 6.90 (1H, dd, J = 8.5, 2.1 Hz, H-6), 6.70 (1H, s, H-3); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 176.6 (C-4), 162.9 (C-7), 162.8 (C-2), 161.0 (C-4′), 157.7 (C-9), 128.5 (C-2′, C-6′), 126.8 (C-5), 122.2 (C-1′), 116.5 (C-10), 116.3 (C-3′, C-5′), 115.1 (C-6), 104.9 (C-3), 102.8 (C-8). These data were consistent with those of reference (Yu and Yang, 1999).

Compound **10**: yellow amorphous powder; ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 12.98 (1H, s, OH-5), 10.77 (1H, s, OH), 10.08 (1H, s, OH), 7.58 (1H, brd, J = 8.9 Hz, H-6′), 7.57 (1H, brs, H-2′), 6.94 (1H, d, J = 8.9 Hz, H-5′), 6.92 (1H, s, H-3), 6.52 (1H, d, J = 1.6 Hz, H-8), 6.20 (1H, d, J = 1.6 Hz, H-6), 3.90 (3H, s, OMe); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 182.7 (C-4), 165.0 (C-7), 164.5 (C-2), 162.3 (C-5), 158.2 (C-9), 151.6 (C-3′), 148.9 (C-4′), 122.4 (C-6′), 121.2 (C-1′), 116.6 (C-5′), 111.1 (C-2′), 104.6 (C-10), 104.1 (C-3), 99.7 (C-6), 94.9 (C-8). These data were consistent with those of reference (Yu and Yang, 1999).

Discussion

Compound **1** was isolated as colorless oil and its molecular formula was assigned as $C_{16}H_{28}O_3$ by analyses of ESI–MS at *m/z* 269 $[M + H]^+$, 291 $[M + Na]^+$. The IR spectrum revealed hydroxy (3 480 cm^{-1}), carbonyl (1 710 cm^{-1}) and double bond (1 647 cm^{-1}) functionalities. The ^{1}H-NMR data (Table 1) indicated three terminal olefinic proton signals at δ 5.24 (1H, brd, J = 17.3 Hz), 5.10 (1H, brd, J = 10.8 Hz), 5.92 (1H, dd, J = 17.3, 10.8 Hz) forming an AMX system; an olefinic proton on a tri-substituted double bond at δ 6.75 (1H, brt, J = 7.4 Hz); two oxymethylene protons at δ 4.01 (1H, dd, J = 10.8, 6.0 Hz), 3.92 (1H, dd, J = 10.8, 6.6 Hz); four regular methylene groups at δ 1.73, 1.65, 1.45, and 1.24 (each 2H, m); as well as signals of four methyl groups at δ 1.83 (3H, s), 1.32 (3H, s), 0.93 (3H, d, J = 7.4 Hz), and 0.92 (3H, t, J = 7.5 Hz). A -CH_2CH

(CH_3) $CH_2CH_2CH_3$ group, a CH_2=CH- group, and a -CH_2CH_2CH= fragment were confirmed by ^{1}H-^{1}H COSY correlations (Fig. 2). The 16 signals of the ^{13}C-NMR spectrum and a DEPT experiment (Table 1) of compound **1** showed the corresponding carbon signals and in addition one carbonyl at δ 168.7, one quaternary carbon at δ 128.4 and one oxygen-bearing quaternary carbon at δ 73.5. The ^{1}H and ^{13}C-NMR data of compound **1** were very similar to those of (2*E*, 6*S*)-6-hydroxy-2, 6-dimethyl-2, 7-octadienoic acid (Alberto *et al*, 1993) except for one more 2-methylpentanol moiety presented in compound **1**. In HMBC spectrum, the correlations between the protons of H-1′ at δ 4.01 (1H, dd, J = 10.8, 6.0 Hz), 3.92 (1H, dd, J = 10.8, 6.6 Hz), and carbon signal at δ 168.7 (C-1) indicated 2-methylpentanol moiety connected with C-1 through an ester linkage in compound **1**. The absolute stereochemistry of compound **1** was under deducing. However, no matter the stereochemistry is *S* or *R*, it is still a new compound.

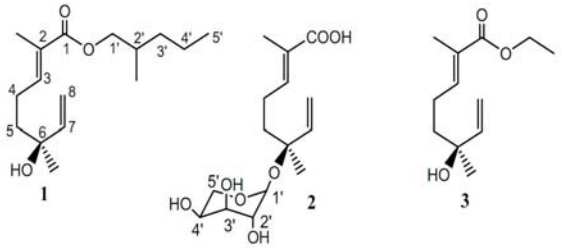

Fig. 1 Structures of compounds 1–3

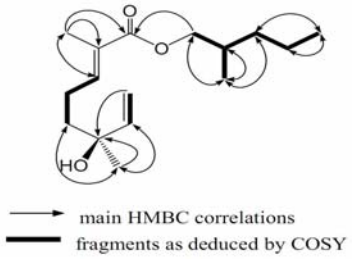

Fig. 2 HMBC and COSY correlations of compound 1

Compound **3** was synthesized in 1995 (Carda *et al*, 1995) and no report has been found that compound **3** was isolated from natural source. Compound **4** was synthesized in 1965 (Jain *et al*, 1965), and was reported from plants *Apuleia leiocarpa* (Vog.) Macbr and *Chrysosplenium grayanum* Maxim (Braz and Gottlieb,

Table 1 ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz) data of compounds 1-3; δ in ppm and J in Hz

No.	**1**[a]		**2**[b]		**3**[a]	
	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	168.7		168.2	12.1 brs, COOH	168.6	
2	128.4		126.9		128.3	
3	142.3	6.75 1H, brt, 7.4	142.3	6.63 1H, brt, 7.5	142.3	6.75 1H, brt, 7.5
4	23.8	2.22 2H, m	22.5	2.20 2H, m	23.8	2.21 2H, m
5	41.1	1.65 2H, m	39.3	1.60 2H, m	41.0	1.64 2H, m
6	73.5		77.8		73.5	
7	144.9	5.92 1H, dd, 17.3, 10.8	144.0	5.90 1H, dd, 17.7, 11.0	144.9	5.91 1H, dd, 17.4, 10.8
8	112.6	5.24 1H, brd, 17.3 5.10 1H, brd, 10.8	115.0	5.23 1H, brd, 17.7 5.15 1H, brd, 11.0	112.6	5.23 1H, brd, 17.4 5.09 1H, brd, 10.8
2-Me	12.8	1.83 3H, s	11.5	1.33 3H, s	12.7	1.82 3H, s
6-Me	28.5	1.32 3H, s	22.2	1.27 3H, s	28.4	1.31 3H, s
1′	69.5	4.01 1H, dd, 10.8 6.0 3.92 1H, dd, 10.8 6.6	97.8	4.79 1H, brs	60.8	4.16 2H, q, 7.5
2′	34.7	1.73 1H, m	70.2	3.58 1H, m[c]	14.7	1.28 3H, t, 7.5
3′	28.4	1.45 2H, m	72.7	3.32 1H, m[c]		
4′	26.6	1.24 2H, m	67.1	4.15 1H, m		
5′	11.7	0.92 3H, t, 7.5	64.6	3.60 1H, m[c] 3.35 1H, m[c]		
2′-Me	16.9	0.93 3H, d, 7.4				

a in $CDCl_3$; b in DMSO-d_6; c overlapped

1971, Arisawa *et al*, 1991). As no ^{13}C-NMR assignments of compounds **3** and **4** have been reported so far, we gave the complete assignment of ^{13}C-NMR data of compounds **3** and **4** by COSY, HMQC, and HMBC spectra (see identification). Compounds **4**–**10** were isolated from *G. chinensis* for the first time.

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