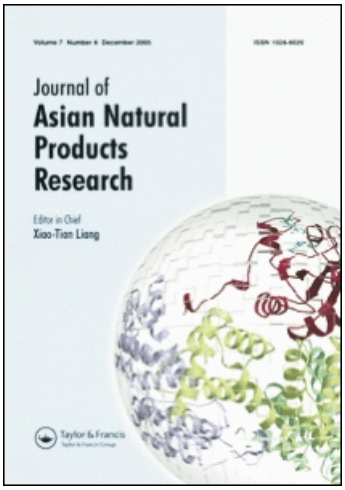

Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

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To cite this Article Li, Shuai , Kuang, Hai-Xue , Okada, Yoshihito and Okuyama, Toru(2005) 'New flavanone and chalcone glucosides from Bidens bipinnata Linn.', Journal of Asian Natural Products Research, 7: 1, 67 — 70
To link to this Article: DOI: 10.1080/10286020310001617147
URL: http://dx.doi.org/10.1080/10286020310001617147

Journal of Asian Natural Products Research, Vol. 7, No. 1, February 2005, 67–70

New flavanone and chalcone glucosides from *Bidens bipinnata* Linn.

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(Received 24 April 2003; revised 3 June 2003; in final form 5 June 2003)

A new flavanone glucoside, bidenoside F, and a new chalcone glucoside, bidenoside G, along with the known compound iso-okanin 7-*O*-(4″,6″-diacetyl)-β-D-glucopyranoside have been isolated from the aerial parts of *Bidens bipinnata* L. The structures were determined on the basis of spectroscopic methods.

Keywords: *Bidens bipinnata*; Bidenoside F; Bidenoside G; Flavonoids

1. Introduction

Bidens bipinnata Linn., a weed of the Compositae family, is widely distributed in China. It has been used as a folk medicine against various diseases, such as inflammations, rheumatism, sore throat, hypertension and diabetes [1]. We report here on the isolation and structural elucidation of a new flavanone glucoside, bidenoside F (**1**), and a chalcone glucoside, bidenoside G (**2**).

2. Results and discussion

Compound **1** (bidenoside F) a light yellow powder, and has a molecular formula $C_{25}H_{26}O_{13}$ by analysis of the positive HR-FABMS. It has a UV absorption band typical of a flavanone, the maxima appears at λ_{max} 276 nm. ^{1}H NMR signals at δ 6.98 (1H, d, $J = 2.0$ Hz), 6.79 (1H, d, $J = 8.2$ Hz), 6.84 (1H, dd, $J = 8.2$, 2.0 Hz) and δ 7.37 (1H, d, $J = 9.0$ Hz), 6.86 (1H, d, $J = 9.0$ Hz) indicate a flavanone with a 3′,4′-disubstituted B-ring and two *ortho*-H atoms in the A-ring. The signals at δ 5.40 (1H, dd, $J = 13.0$, 3.0 Hz), 3.10 (1H, dd, $J = 17.0$, 13.0 Hz) and 2.79 (1H, dd, $J = 17.0$, 3.0 Hz) reveal the H-2 and H-3 in C-ring of

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Journal of Asian Natural Products Research
ISSN 1028-6020 print/ISSN 1477-2213 online © 2005 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/10286020310001617147

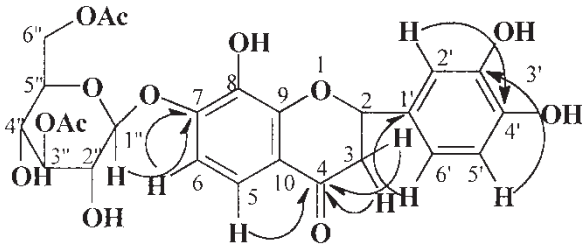

Figure 1. The key HMBC correlations of **1**.

the flavanone. This suggested that **1** is an iso-okanin glucoside having two acetyl groups in the glucose moiety. The ^{13}C NMR signals of the aglycone moiety are identical with those of iso-okanin 7-*O*-β-D-glucopyranoside (**3**) [2]. The acylation sites were readily inferred from the downfield shift of the H-3″ (δ 5.04) and 6″ signals (δ 4.26 and 4.41). In the ^{13}C NMR spectrum of **1** the sugar carbon signals assignable to C-2″, 4″ and 5″ were shifted upfield, and the C-3″ and C-6″ shifted downfield compared with those of **3**. These changes suggest that the C-3″ and C-6″ hydroxyls of the glucose are acetylated. Thus, **1** was determined as iso-okanin 7-*O*-(3″,6″-diacetyl)-β-D-glucopyranoside.

The complete assignments of ^{1}H and ^{13}C NMR spectral data for **1** were achieved on the basis of 2D DQF-COSY, HMQC and HMBC spectra (figure 1). The configuration of C-2 for **1** is still under investigation.

Compound **2** (bidenoside G) was obtained as an orange powder, and the molecular formula $C_{23}H_{24}O_{11}$ was assigned by the HR-FABMS measurement. It exhibited a major UV absorption band typical of a chalcone at λ_{max} 369 nm. A bathochromic shift of 53 nm after the addition of aluminium chloride and hydrochloric acid indicated the presence of a free 2′-hydroxyl group. The ^{1}H and ^{13}C NMR signals are very similar to those of okanin 4′-*O*-(6″-*O*-acetyl)-β-D-glucopyranoside (**4**) [3]. In the ^{1}H NMR spectrum, the signals at δ 7.10 (1H, d, $J = 2.1$ Hz), 6.72 (1H, d, $J = 8.2$ Hz) and 7.03 (1H, dd, $J = 8.2$, 2.1 Hz) indicate a chalcone skeleton with a 3′,4′-substituted B-ring, δ 6.70 (1H, d, $J = 2.7$ Hz), 6.68 (1H, dd, $J = 9.1$, 2.7 Hz) and 7.52 (1H, d, $J = 9.1$ Hz) signals show an ABX system in the A-ring, and the signals at δ 7.46 (1H, d, $J = 15.2$ Hz) and 7.67 (1H, d, $J = 15.2$ Hz) are due to the α,β-protons of chalcone. The signal at δ 1.91 is from an acetyl group attached to the sugar moiety. The chemical shift of H-6″ is shifted downfield (δ 4.16 and 4.32) compared with that of the glucose, suggesting that the acetyl group is at C-6″. The chemical shift of C-3′ of the A-ring, further upfield (δ 119.5) than that of compound **4**, proved to be a methine, suggesting that C-3′ is not substituted by an hydroxyl. This was further confirmed by the coupling constants of the proton signals of A-ring. Thus **2** was determined as 3,4,2′-trihydroxychalcone-4′-*O*-(6″-*O*-acetyl)-β-D-glucopyranoside (figure 2).

3. Experimental

3.1 General experimental procedures

Melting points were measured on a Yanagimoto melting point apparatus and are uncorrected. UV spectra were taken in MeOH on a Shimadzu UV 260 spectrometer. IR spectra were obtained with a Hitachi 557 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on

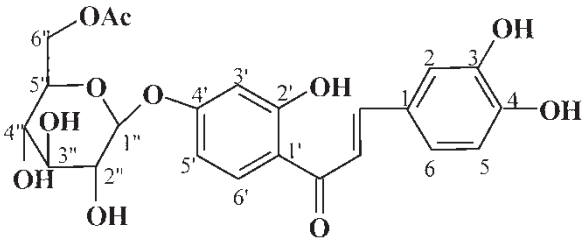

Figure 2. The structure of **2**.

a JNM-LA 500 spectrometer. FAB-MS spectra were measured on a JMS-DX 302 mass spectrometer. Optical rotations were determined in MeOH on a JASCO DIP-140 polarimeter. Preparative HPLC was performed on a Hitachi (L-6000 pump) instrument with a Waters 5 C_{18}-AR-II column (10 × 250 mm) and Waters 5 SL (10 × 250 mm). Detector: UV SSC-5200.

3.2 Plant material

The aerial parts of *Bidens bipinnata* were collected from the wild fields of Heilongjiang Province, China, in September 1998 and were identified by Professor Gui-Jun Zhang. A specimen has been deposited at the Chinese Medicine Museum of Heilongjiang University of Traditional Chinese Medicine, Harbin, China.

3.3 Extraction and isolation

The air-dried aerial parts (4 kg) of *Bidens bipinnata* L. were extracted twice with hot 95% EtOH for 2 h and the combined EtOH extract was concentrated *in vacuo* to give a syrup (323 g), followed by suspension in water. The suspension was then extracted with n-hexane, ethyl acetate and n-butanol successively. The EtOAc extract (20 g) was chromatographed on silica gel column and eluted with n-hexane–EtOAc (8:2) and (4:6) gradiently eluted to give 12 fractions (Fr. 1–12). Fraction 7 (1.5 g) was subjected to column chromatography over silica gel, eluting with n-hexane–EtOAc (4:6) and (2:8) to give 5 further fractions. Fraction 2 (0.6 g) was subjected to reversed-phase (ODS) column chromatography, followed by preparative HPLC (EtOAc–Me_2CO–H_2O, 6:0.5:0.1) to afford **1** (8.3 mg) and **2** (7.6 mg).

3.3.1 Bidenoside F (1). A light yellow powder (MeOH), mp 172–174°C; $[\alpha]_D^{25}$ −15.2 ($c = 0.16$, MeOH). FAB-MS (positive) *m/z*: 535 $[M + 1]^+$, 289 [aglycone + H]$^+$, 229, 169, 153. HR-FABMS *m/z*: 535.1404 ($[M + H]^+$, calcd for $C_{25}H_{27}O_{13}$, 535.1451). UV λ_{max} (MeOH) nm (log ε): 225 (4.36), 276 (4.02); +NaOMe: 252, 296, 375; +NaOAc: 289; + $AlCl_3$: 232, 287, 314; +$AlCl_3$ + HCl: 280, 324, 418. IR ν_{max} KBr (cm^{-1}): 3420, 1735, 1652, 1600, 1443, 1360, 1235. ^{1}H NMR (CD_3OD) δ: (ppm): 5.40 (1H, dd, $J = 13.0$, 3.0 Hz, H-2), 2.79 (1H, dd, $J = 17.0$, 3.0 Hz, H-3a), 3.10 (1H, dd, $J = 17.0$, 13.0 Hz, H-3b), 7.37 (1H, d, $J = 9.0$ Hz, H-5), 6.86 (1H, d, $J = 9.0$ Hz, H-6), 6.98 (1H, d, $J = 2.0$ Hz, H-2′), 6.79 (1H, d, $J = 8.2$ Hz, H-5′), 6.84 (1H, dd, $J = 8.2$, 2.0 Hz, H-6′), 5.06 (1H, d, $J = 7.9$ Hz, H-1″), 3.68 (1H, dd, $J = 8.4$, 7.9 Hz, H-2″), 5.04

(1H, dd, $J = 9.5$, 8.4 Hz, H-3″), 3.55 (1H, dd, $J = 9.5$, 9.6 Hz, H-4″), 3.78 (1H, m, H-5″), 4.26 (1H, dd, $J = 12.0$, 6.4 Hz, H-6″a), 4.41 (1H, dd, $J = 12.0$, 2.7 Hz, H-6″b), 2.05 and 2.13 (each 3H, s, OAc). ^{13}C NMR (CD_3OD) δ (ppm): 81.7 (C-2), 45.2 (C-3), 194.1 (C-4), 118.6 (C-5), 110.8 (C-6), 152.5 (C-7), 136.7 (C-8), 152.0 (C-9), 118.3 (C-10), 131.8 (C-1′), 115.1 (C-2′), 146.5 (C-3′), 147.0 (C-4′), 116.3 (C-5′), 119.6 (C-6′). Glucose: 102.4 (C-1″), 73.0 (C-2″), 78.2 (C-3″), 69.9 (C-4″), 75.5 (C-5″), 64.4 (C-6″); 172.6 and 172.5 (C═O, OAc), 20.7 and 21.1 (CH_3,OAc).

3.3.2 Bidenoside G (2). A yellow powder (MeOH), mp 202–204°C; $[\alpha]_D^{25}$ −71.2 ($c = 0.15$, MeOH). FAB-MS (positive) *m/z* 477 $[M + 1]^+$, 273 [aglycone + H]$^+$, 229, 169, 153, 136. HR-FABMS *m/z*: 477.1354 ($[M + H]^+$, calcd for $C_{23}H_{25}O_{11}$, 477.1396). UV (MeOH) λ_{max} nm (log ε): 261(3.85), 369(4.42); +NaOMe: 283, 352; +NaOAc: 257, 370; +$AlCl_3$: 240, 268, 476; +$AlCl_3$ + HCl: 240, 268, 422. IR ν_{max} KBr (cm^{-1}): 3422, 1738, 1640, 1570, 1500, 1440, 1280. ^{1}H NMR (CD_3OD) δ ppm 7.46 (1H, d, $J = 15.2$ Hz, H-α), 7.67 (1H, d, $J = 15.2$ Hz, H-β), 7.10 (1H, d, $J = 2.1$ Hz, H-2), 6.72 (1H, d, $J = 8.2$ Hz, H-5), 7.03 (1H, dd, $J = 8.2$, 2.1 Hz, H-6), 6.70 (1H, d, $J = 2.7$ Hz, H-3′), 6.68 (1H, dd, $J = 9.1$, 2.7 Hz, H-5′), 7.52 (1H, d, $J = 9.1$ Hz, H-6′), 4.89 (1H, d, $J = 7.3$ Hz, H-1″), 3.44 (1H, dd, $J = 8.6$, 7.3 Hz, H-2″), 3.41 (1H, dd, $J = 9.0$, 8.6 Hz, H-3″), 3.32 (1H, dd, $J = 9.2$, 9.0 Hz, H-4″), 3.60 (1H, m, H-5″), 4.16 (1H, dd, $J = 12.0$, 6.2 Hz, H-6″a), 4.32 (1H, dd, $J = 12.0$, 2.1 Hz, H-6″b), 1.91 (3H, s, CH_3, OAc). ^{13}C NMR (CD_3OD) δ (ppm): 128.3 (C-1), 116.0 (C-2), 146.9 (C-3), 150.2 (C-4), 116.7 (C-5), 123.9 (C-6), 194.6 (C═O), 118.3 (α-C), 147.0 (β-C), 117.5 (C-1′), 146.5 (C-2′), 119.5 (C-3′), 151.5 (C-4′), 108.1(C-5′), 122.4 (C-6′). Glucose: 102.5 (C-1″), 74.7 (C-2″), 77.4 (C-3″), 71.5 (C-4″), 75.6 (C-5″), 64.6 (C-6″); 172.7 (C═O, OAc) and 20.5 (CH_3, OAc).

Acknowledgements

We thank Ms Omae for obtaining the NMR spectra and Ms Koseki for the measurement of MS spectra.

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