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New Acetylenic Glucosides from *Bidens bipinnata* LINNE

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Two new acetylenic glucosides, 8*Z*-decaene-4,6-diyn-1-*O*-β-D-glucopyranoside named bidenoside C, and 8*E*-decaene-4,6-diyn-3,10-dihydroxy-1-*O*-β-D-glucopyranoside named bidenoside D, have been isolated from the aerial parts of *Bidens bipinnata* LINNE (Asterceae). These structures have been elucidated on the basis of spectroscopic methods.

Key words *Bidens bipinnata*; acetylenic compound; Asterceae; bidenoside C; bidenoside D

Bidens bipinnata LINNE, a weed of the Asterceae family, is widely distributed in China. It has been used as a folk medicine against various diseases such as inflammation, rheumatism, sore throat, hypertension and diabetes.[1)] We reported the isolation and structural elucidation of seven flavonoids in the EtOH extract of *B. bipinnata*.[2)] In order to continue our studies on this herb, we now report the isolation and structural elucidation of two new acetylenic glucosides, bidenoside C (**1**) and D (**2**).

Bidenoside C (**1**), a colorless syrup, with the molecular formula $C_{16}H_{22}O_6$, was established by HR (high-resolution)-FAB-MS (*m/z* 311.1529, $[M+H]^+$). The IR spectrum of **1** exhibited the presence of a hydroxyl at 3380 cm^{-1} (OH), and 2218 and 2162 cm^{-1} (–C≡C–), 1630 cm^{-1} (–C=C–). The ^1H- and ^{13}C-NMR spectra showed the presence of a glucopyranosyl unit [δ_H 4.25 (anomeric proton), δ_C 104.5, 78.1, 78.0, 75.1, 71.7, 62.8]. The anomeric proton at 4.25 ppm (d, $J=7.6$ Hz) for H-1′ in the ^1H-NMR spectrum indicated β-D-glucose. The ^{13}C-NMR spectrum showed four quaternary carbon signals at δ_C 66.1, 72.5, 77.9 and 85.1 ppm, suggesting the presence of two pairs of triple bonds, and six other signals (δ_C 16.3, 16.9, 29.8, 69.2, 110.0, 143.0). Each carbon signal was respectively connected to methyl at δ_H 1.86 (3H, dd, $J=6.9$, 1.7 Hz), methylene at δ_H 2.48 (2H, t, $J=7.0$ Hz) and at δ_H 1.84 (2H, t, $J=7.0$ Hz), oxymethylene at δ_H 3.64 (1H, dt, $J=10.1$, 6.2 Hz) and 3.96 (1H, dt, $J=10.1$, 6.2 Hz), and the olefinic protons at δ_H 5.50 (1H, m) and 6.13 (1H, dq, $J=10.9$, 6.9 Hz) in the heteronuclear multiple quantum coherence (HMQC) spectrum. The connections of the carbons were determined by analyses of the ^1H–^1H correlated spectroscopy (COSY) spectrum and by means of a proton decoupling experiment. The coupling constant ($J=10.9$ Hz) of the olefinic protons showed that the configuration of the double bond is *Z*. The locations of two triple bonds were determined as follows: there is no correlation between δ_H 2.48 and 5.50, and the anomeric carbon at δ_C 104.5 and methylene carbon at δ_C 69.2 both bear an oxygen atom. Furthermore, by the comparison of chemical shifts with similar compounds,[3)] bidenoside C was established to be 8*Z*-decaene-4,6-diyn-1-*O*-β-D-glucopyranoside.

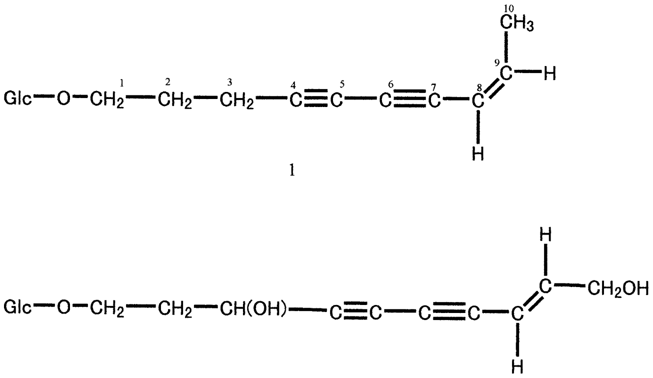
Bidenoside D (**2**) was obtained as a colorless syrup. The HR-FAB-MS established that the molecular formula was $C_{16}H_{22}O_8$ (*m/z* 343.1440). By the comparison of ^1H- and ^{13}C-NMR spectral data with those of **1**, it was suggested that **2** also has two acetylenic bonds in its molecule. The connectivity of the carbons in aglycone was determined by analysis of the ^1H–^1H COSY spectrum and by means of a proton decoupling experiment. From the coupling constant ($J=15.9$ Hz) of the olefinic protons, the configuration of the double bond is *E*. The locations of triple bonds were determined in the same manner. Thus, bidenoside D can be formulated as 8*E*-decaene-4,6-diyn-3,10-dihydroxy-1-*O*-β-D-glucopyranoside.

Experimental

General Procedure The optical rotations were measured with a Perkin-Elmer 241 Polarimeter. ^1H- and ^{13}C-NMR spectra were taken with a JEOL JNM-LA 500 spectrometer in CD_3OD. Chemical shifts are given in δ values (ppm), with TMS as an internal standard. FAB-MS spectra were recorded with a Micross Mass Autospec-UltimaE TOF mass spectrometer. IR spectra were measured with a NICOLET Impact 400 spectrophotometer. 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: RI ERC-7520.

Plant Materials The aerial parts of *Bidens bipinnata* LINNE were collected from a wild field in Heilongjiang Province on September 1998, in China. The plant was identified by Prof. Gui-jun Zhang, and the voucher specimen has been deposited at the Chinese Medicine Museum of Heilongjiang University of Traditional Chinese Medicine, Harbin, China.

Extraction and Isolation The air-dried aerial part (4 kg) of *B. bipinnata* LINNE was extracted twice with hot 95% EtOH (10 l) for 2 h, and the combined solution was concentrated *in vacuo* to a syrup (323 g), followed by suspension in water. The suspension was extracted with *n*-hexane, ethyl acetate and then *n*-butanol. The *n*-butanol extract (50 g) was chromatographed on silica gel and eluted successively with an EtOAc–MeOH gradient elute to give 10 fractions (Fr. 1—10). Fraction No. 2 (4.2 g) was subjected to reversed-phase (ODS) column chromatography and eluted with 30% aqueous



$$\mathrm{Glc{-}O{-}\overset{1}{C}H_2{-}\overset{2}{C}H_2{-}\overset{3}{C}H_2{-}\overset{4}{C}{\equiv}\overset{5}{C}{-}\overset{6}{C}{\equiv}\overset{7}{C}{-}\overset{8}{C}H{=}\overset{9}{C}H{-}\overset{10}{C}H_3}$$

1

$$\mathrm{Glc{-}O{-}CH_2{-}CH_2{-}CH(OH){-}C{\equiv}C{-}C{\equiv}C{-}CH{=}CH{-}CH_2OH}$$

2

Fig. 1. Structures of **1** and **2**

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Table 1. ^{1}H-NMR Spectral Data for Compounds **1** and **2**$^{a)}$

	1	**2**
1	3.64 (1H, dt, J=10.1, 6.2)	3.73 (1H, dt, J=10.2, 6.4)
	3.96 (1H, dt, J=10.1, 6.2)	3.99 (1H, dt, J=10.2, 5.8)
2	1.84 (2H, t, J=7.0)	1.97 (2H, ddd, J=6.7, 6.4, 5.8)
3	2.48 (2H, t, J=7.0)	4.64 (1H, t, J=6.7)
8	5.50 (1H, m)	5.80 (1H, dtd, J=15.9, 0.9, 2.1)
9	6.13 (1H, dq, J=10.9, 6.9)	6.39 (1H,dt, J=15.9, 4.8)
10	1.86 (3H, dd, J=6.9, 1.7)	4.13 (2H, dd, J=4.8, 2.1)
1′	4.25 (1H, d, J=7.6)	4.26 (1H, d, J=7.9)

a) ppm from TMS, J=Hz, in CD_3OD, 500 MHz, room temperature.

Table 2. ^{13}C-NMR Spectral Data for Compounds **1** and **2**$^{a)}$

	1	**2**
1	69.2 t	67.0 t
2	29.8 t	39.1 t
3	16.9 t	60.4 d
4	66.1 s	69.7 s
5	72.5 s	74.3 s
6	77.9 s	77.8 s
7	85.1 s	84.5 s
8	110.0 d	108.8 d
9	143.0 d	148.2 d
10	16.3 q	62.8 t
1′	104.5 d	104.8 d
2′	75.1 d	75.3 d
3′	78.1 d	78.3 d
4′	71.7 d	71.8 d
5′	78.0 d	78.1 d
6′	62.8 t	63.0 t

a) ppm from TMS, in CD_3OD, 125 MHz, room temperature.

MeOH to give 5 fractions (I—V). Fraction IV was purified by preparative HPLC-ODS (50% aqueous MeOH) to afford **1** (6.2 mg). Fraction No. 3 (5.6 g) was subjected to reversed-phase (ODS) column chromatography eluted with 20% aqueous MeOH to give 6 fractions (I—V). Fraction IV was purified by Sephadex LH-20, and eluted with MeOH, followed by preparative HPLC-ODS with 25% aqueous MeOH to afford **2** (11 mg).

Bidenoside C (8*Z*-Decaene-4,6-diyn-1-*O*-β-D-glucopyranoside) (**1**): A colorless syrup, $[\alpha]_D^{25}$ $-18°$ (c=0.10, MeOH), HR-FAB-MS *m*/*z*: obs. 311.1529 $[M+H]^+$ (Calcd for $C_{16}H_{23}O_6$: 311.1494). IR (KBr) cm^{-1}: 3380 (OH), 2218 (–C≡C–), 2162 (–C≡C–), 1630 (–C=C–), 1375, 1226, 1028. ^{1}H- and ^{13}C-NMR spectra are shown in Tables 1 and 2.

Bidenoside D (8*E*-Decaene-4,6-diyn-3,10-dihydroxy-1-*O*-D-glucopyranoside) (**2**): A colorless syrup, $[\alpha]_D^{25}$ $-27°$ (c=0.10, MeOH), HR-FAB-MS *m*/*z*: 343.1440 $[M+H]^+$ (Calcd for $C_{16}H_{23}O_8$. 343.1392). IR (KBr) cm^{-1}: 3320 (OH), 2216 (–C≡C–), 2164 (–C≡C–), 1628 (–C=C–), 1375, 1225, 1036. ^{1}H- and ^{13}C-NMR spectra are shown in Tables 1 and 2.

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