Chinese Chemical Letters Vol. 13, No. 4, pp. 337-340, 2002 337
http://www.imm.ac.cn/journal/ccl.html

Two New C-glucoside Flavonoids from Leaves of *Crataegus pinnatifida* Bge. var. *major* N. E. Br.

Pei Cheng ZHANG[1]*, Sui Xu XU[2]

[1] Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing 100050
[2] Department of Phytochemistry, Shenyang Pharmaceutical University, Shenyang 110015

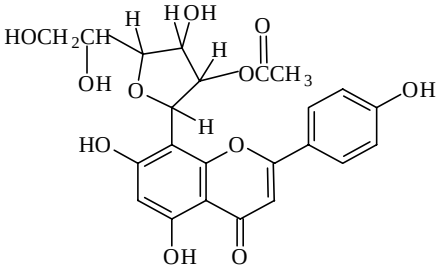
Abstract: Two new C-glucoside flavonoids, namely 8-C-*β*-D-(2″-O-acetyl) glucofuranosyl apigenin and 3″-O-acetylvitexin, were isolated from leaves of *Crataegus pinnatifida* Bge. var. *major* N. E. Br.. Their structures were elucidated by the spectroscopic means and chemical evidence.

Keywords: *Crataegus pinnatifida* Bge. var. *major* N. E. Br., Rosaceae, 8-C-*β*-D-(2″-O-acetyl) gluco furanosyl apigenin, 3″-O-acetylvitexin.

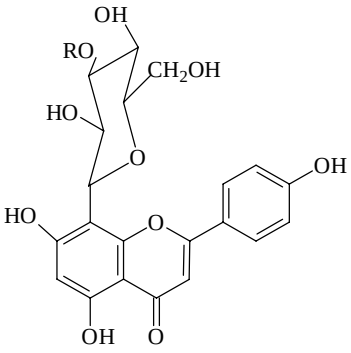
Crataegus pinnatifida Bge. var. *major* N. E. Br. (*Rosaceae*) is widely distributed in the northeast part of China. It is used as medicine plant to improve digestion, remove retention of food, promote blood circulation and resolve blood stasis both in official and traditional folk medicine[1]. Preparations of *Crataegus pinnatifida* Bge. var. *major* (leaves or fruit) improve the heart function, and their indications are cases of declining cardiac performance, deficiency of the coronary blood supply and mild forms of arrhythmia[2,3]. Up to now, about fifty flavonoids have been isolated from *Crataegus*[4,5]. In our study on the chemical constituents of the leaves of this plant six C-glucoside flavonoids were isolated including two new compounds, named 8-C-β-D-(2″-O-acetyl) gluco furanosyl apigenin (**1**) and 3″-O-acetylvitexin (**2**).

Compound **1** was obtained as yellow needles, mp 220-222°C, $[\alpha]_D^{25}$: +63.2 (c 0.10, MeOH) and exhibiting a positive ferric chloride test and magnesium hydrochloric acid test. The HRFABMS of **1** indicated a molecular ion peak at *m/z* 474.1151 (calc. 474.1162), which corresponded to a molecular formula $C_{23}H_{22}O_{11}$. The absorption bands at ν 3370, 1710, 1650, 1606, and 1520 cm^{-1} in the IR spectrum were characteristics of hydroxyl, hydrogen bonded carbonyl, unconjugated carbonyl, and aromatic groups, respectively. The UV spectrum of **1** exhibited absorption maxima at 333 (Band I) and 270 nm (Band II) (in MeOH), bathochromic shifts of 57, 43 and 47 nm with NaOMe, NaOAc and $AlCl_3$ in Band I, respectively, as well as bathochromic shifts of 7 nm with NaOMe and NaOAc and $AlCl_3$ in Band II. These data revealed that **1** has a typical apigenin-type structure.

*E-mail: pczhang@ imm.ac.cn



1



2 R = Acetyl

3 R=H vitexin

The ^{1}H-NMR of **1** (**Table 1**) showed an aromatic hydroxyl signal at δ 13.81(5-OH), a 4′-hydroxylphenyl group [8.00, 7.27 (d, each 2H, *J*=8.8 Hz)], and two aromatic proton signals at δ 6.72 (s, H-6) and δ 6.91 (s, H-3). The ^{13}C-NMR data (**Table 2**) showed 23 signals, including a flavonoid nucleus, a saccharide moiety and an acetyl group. In the DEPT spectrum six carbon signals of sugar moiety were at δ 85.4 (CH), 82.6 (CH), 79.2 (CH), 75.5 (CH), 70.1 (CH) and 65.3 (CH_2), indicating that **1** was C-glucoside flavonoid. The site of the sugar linkage to the aglycone in **1** was considered to be at the C-8 position by the appearance of the cross peaks of the anomeric proton of the sugar at δ_H 6.03 (d, *J*=3.1 Hz, H-1″) with the carbons at δ_C 163.6 (C-7), 105,0 (C-8), and 155.5 (C-9) in the HMBC spectrum. In the same time, the proton and carbon signals of the sugar moiety were at lower field, and the $J_{H\text{-}H}$ values were smaller (about 3 Hz) compared with the corresponding signal of vitexin[6], which suggested that the sugar was furanose form in association with the ^{1}H-^{1}HCOSY, NOESY and HMBC spectra. In the NOESY spectrum, the signals at δ_H 6.03 (H-1″) and δ_H 4.63 (H-4″) show corroelation to H-3″ (δ_H 5.10), indicating the sugar was β–D-glucofuranose. Finnally, the position of acetyl group can be confirmed to be C-2″ in sugar moiety by the long distance correlation of δ_C 170.1 and δ_H 5.76 (H-2″). Thus, the structure of **1** was determined as 8-C-β-D-(2″-O-acetyl) glucofuranosylapigenin.

Compound **2** was obtained as yellow powder, mp 194-196°C, $[\alpha]_D^{25}$: -14.6 (c 0.12, MeOH) and exhibiting a positive ferric chloride test and magnesium hydrochloric acid test. The HRFABMS of **2** indicated a molecular ion peak at *m/z* 474.1188 (calc. 474.1162), which corresponded to a molecular formula $C_{23}H_{22}O_{11}$. It was similar to **1** in Mg-HCl color reaction, UV and IR spectra, suggested that **2** also has a 5,7,4′-trihydroxyl flavonoid skeleton. The ^{1}H- (**Table 1**) and ^{13}C-NMR data (**Table 2**) indicated that **2** also was C-8-glucoside flavonoid. The hexose substituent at C-8 gave a pattern of ^{13}C-NMR signals similar to vitexin[6], but the signal of glucose C-3″ appeared at δ_C 79.7, which shifted to the downfield by Δ1.0 ppm compared with the corresponding signal of vitexin (δ_C 78.7). Meanwhile the signals of C-2″ (δ_C 68.5) and C-4″ (δ_C 67.9) of the glucose

showed an upfield shift by Δ 2.4 and Δ 2.7 ppm, respectively, compared with the corresponding signal (δ_C 70.9, 70.6) of vitexin. These suggested that the acetyl group was attached to the C-3″ position of glucose by means of esterification. Furthermore, the sugar functionality also was identified as a *β*-D-glucopyranose by the ^{1}H NMR, ^{1}H-^{1}H, ^{13}C-^{1}HCOSY spectra, and *J* value. Thus, the structure of **2** was formulated to be 3″-O-acetylvitexin.

Table 1 ^{1}H NMR data for compounds **1** (in C_5D_5N), **2** (in DMSO-d_6)

C	**1**	**2**
3	6.91s	6.77s
5	13.81 (OH)	13.16 (OH)
6	6.72 s	6.27s
7		10.95s
2′, 6′	8.00d (8.8)	8.02d (8.8)
3′, 5′	7.27d (8.8)	6.89d (8.8)
Glc-1″	6.03d (3.1)	4.78d (9.7)
2″	5.76d (3.1)	3.97t (9.7)
3″	5.10d (2.4)	4.87t (9.7)
4″	4.63m	3.58m
5″	4.93m	3.58m
6″	4.49-4.31m	3.77m, 3.58m
-CH3	2.02 s	1.96s

Table 2 ^{13}C NMR data for compounds **1** (in C_5D_5N), **2** and **3** (in DMSO-d_6)

C	**1**	**2**	**3**
2	164.3	163.9	164.0
3	104.0	102.5	102.5
4	182.9	181.9	182.1
5	162.8	161.0	161.2
6	101.1	98.0	98.2
7	163.6	162.5	162.6
8	105.0	103.6	104.7
9	155.5	155.9	156.0
10	103.5	103.9	104.1
1′	122.4	121.6	121.7
2′, 6′	129.0	128.9	129.0
3′, 5′	117.0	115.8	115.8
4′	162.6	160.5	160.4
Glc-1″	79.2	73.4	73.4
2″	85.4	68.5	70.9
3″	75.5	79.7	78.7
4″	82.6	67.9	70.6
5″	70.1	81.4	81.9
6″	65.3	60.4	61.3
-CH3	20.8	20.4	
-C=O	170.1	169.8	

References

1. H. Ammon, M. Händel., *Planta Med*, **1981**, *43*, 209.
2. H. Al Makdessi, H. Sweidan, S. Müllner., *Arzneim Forsch Drug Res*, **1996**, *46*, 25.
3. S. Pöpping,, H. Rose, *et al*., *Arzneim Forsch Drug Res*, **1995**, *45*, (Suppl 2), 1157.
4. N. Nikolov, O. Seligmann, *et al*., *Planta Med*, **1982**, *44*, 50.
5. J.C. Dauguet, M. Bert, *et al*., *Phytochemistry*, **1993**, *33*, 1503.
6. L. Lin, N. Xie, H. Cheng., *J. Chin. Pharm. University*, **1999**, *30*, 21.

Received 9 July, 2001