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A New Flavonoid Ketohexofuranoside from Leaves of *Crataegus pinnatifida* Bge.var. *major* N.E.Br.

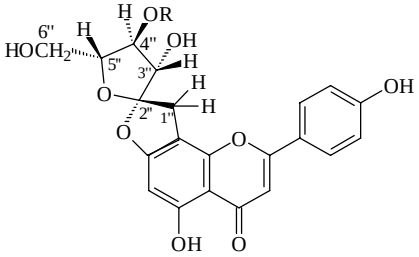
Pei Cheng ZHANG [1]*, Sui Xu XU[2]

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

Abstract: A new flavonoid**,** namely pinnatifine I (**1**), was isolated from the leaves of *Crataegus pinnatifida* Bge. var. *major* N.E.Br.. Its structure was elucidated by spectroscopic analysis and chemical evidence.

Keywords: *Crataegus pinnatifida* Bge.var.*major* N.E.Br., *Rosaceae*, pinnatifine I, flavonoid Ketohexofuranoside,.

Crataegus pinnatifida Bge.var.*major* N.E.Br. is widely distributed in the northeast part of China. It is used as a medicinal plant to improve digestion, remove retention of food, promote blood circulation and resolve blood stasis both in traditional and folk medicine [1]. Preparations of *Crataegus* leaves improve the heart function, the coronary blood supply and arrhythmia[2]. Up to now, fifty flavonoids have been isolated from *Crataegus*[3,4]. In our previous paper, some new flavonoid glycosides were obtained from the leaves of *Crataegus pinnatifida* Bge.var.*major* N.E.Br.. Further chemical investigation has led to the isolation of a new compound from this plant, named pinnatifine I (**1**),



pinnatifine C R=H
pinnatifine I (**1**) R=Acetyl

Compound **1** was obtained as yellow needles and showed positive test to Mg-HCl color reaction. ESIMS exhibited a quasimolecular ion peak at *m/z*: 457 $[M+H]^+$, thus, a

molecular formula of $C_{23}H_{20}O_{10}$ for **1** was deduced in association with the ^{13}C NMR data . The absorption bands at ν 3370, 1710, 1650 and 1606, 1520 cm^{-1} in IR spectrum were characteristics of hydroxyl, carbonyl, chelated carbonyl and aromatic groups, respectively. UV spectrum of **1** exhibited absorption maxima at λmax 326 (Band I) and 271 (Band II) (in MeOH), bathochromic shifts of 66, 41, 66 and 66 nm with NaOMe , NaOAc, $AlCl_3$ and $AlCl_3$+HCl in Band I, respectively, as well as bathochromic shifts of 8 nm with $AlCl_3$ and $AlCl_3$+HCl and no shifts with NaOMe and NaOAc in Band II. These data suggested that **1** had two free hydroxyl groups at C-5, 4′ and no free hydroxyl group at C-7 in the flavone skeleton.

The ^1H NMR spectrum of this compound showed a high field methyl singlet at δ 2.10, a methylene quartet at δ 3.50 (1H, *J*=16.5 Hz) and 3.34 (1H, *J*=16.5 Hz), two aromatic singlets at δ 6.83 and 6.37, a pair of aromatic doublets at δ 7.95 (2H, *J*=8.8 Hz) and 6.92 (2H, *J*=8.8 Hz) characteristic of para-disubstituted aromatic ring, a methine proton at δ 5.08 (1H, m, H-4″), and the signals of the sugar portion in the low field. The ^{13}C NMR spectrum of **1** was similar to that of pinnatifine C (**Table 1**), with two additional carbon signals at δ 20.7, 170.3 indicating the presence of an acetyl group. Furthermore, the position of acetylation was suggested to be at C-4″ by the typical downfield shift of C-4″ at δ 76.0 (Δ δ 2.5) and highfield shift of C-5″ at δ 81.7 (Δ δ 2.0) and C-3″ at δ 77.4 (Δ δ 2.2) in the ^{13}C-NMR spectrum, compared with those of pinnatifine C. Alkaline hydrolysis of **1** with 0.1 % KOH at 60 °C afforded pinnatifine C. Thus, the structure of the compound was elucidated as **1**, named pinnatifine I.

Table 1 ^{13}C NMR data for **1** and pinnatifine C in DMSO-d_6

No	**1**	pinnatifine C	No	**1**	pinnatifine C
2	164.4	164.1	4′	161.3	161.2
3	103.0	102.8	5′	116.0	115.9
4	182.0	181.8	6′	128.6	128.4
5	161.9	161.7	1″	32.6	32.6
6	94.1	93.8	2″	117.7	118.0
7	163.6	163.3	3″	77.4	79.6
8	102.2	102.2	4″	76.0	73.5
9	151.6	151.3	5″	81.7	83.7
10	104.4	104.0	6″	63.4	63.2
1′	121.1	120.9	$-CH_3$	20.7	
2′	128.6	128.4	-C=O	170.3	
3′	116.0	115.9			

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