Supporting Information

***Rec. Nat. Prod*. 11:6 (2017) 514-520**

Prenylated Flavonoids from *Epimedium koreanum* Nakai and their Human Neutrophil Elastase Inhibitory Effects

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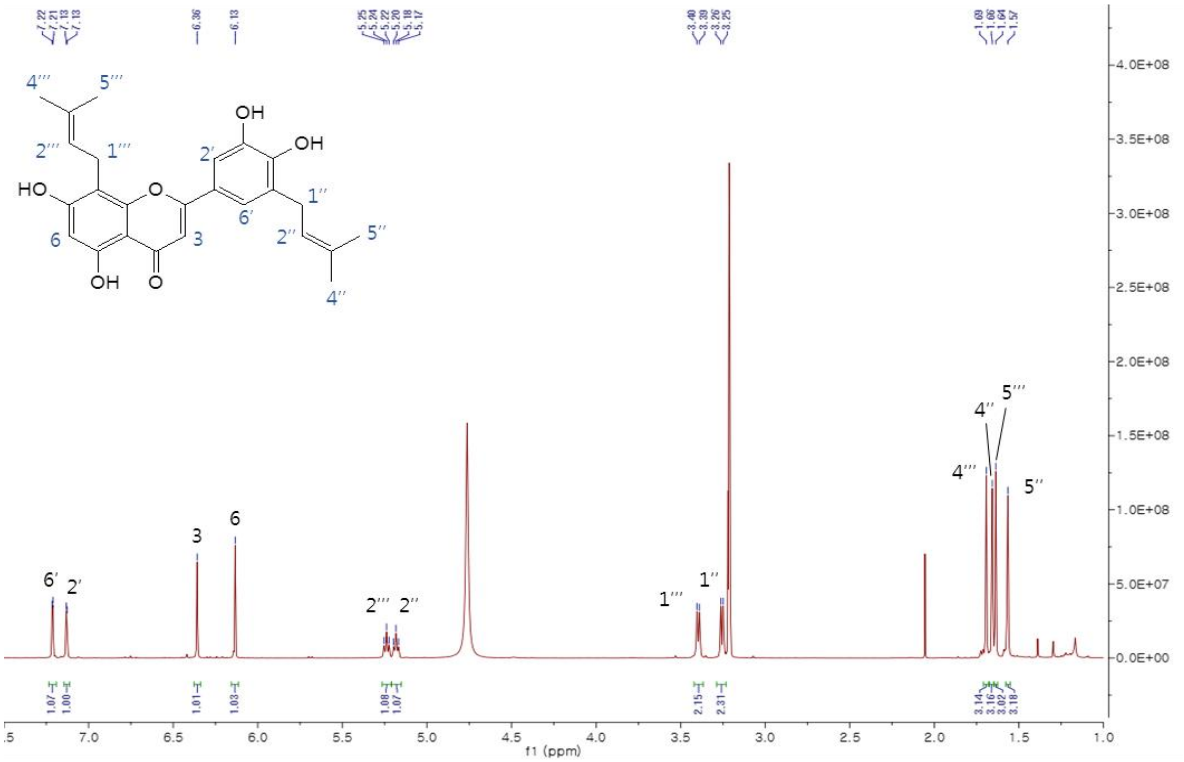
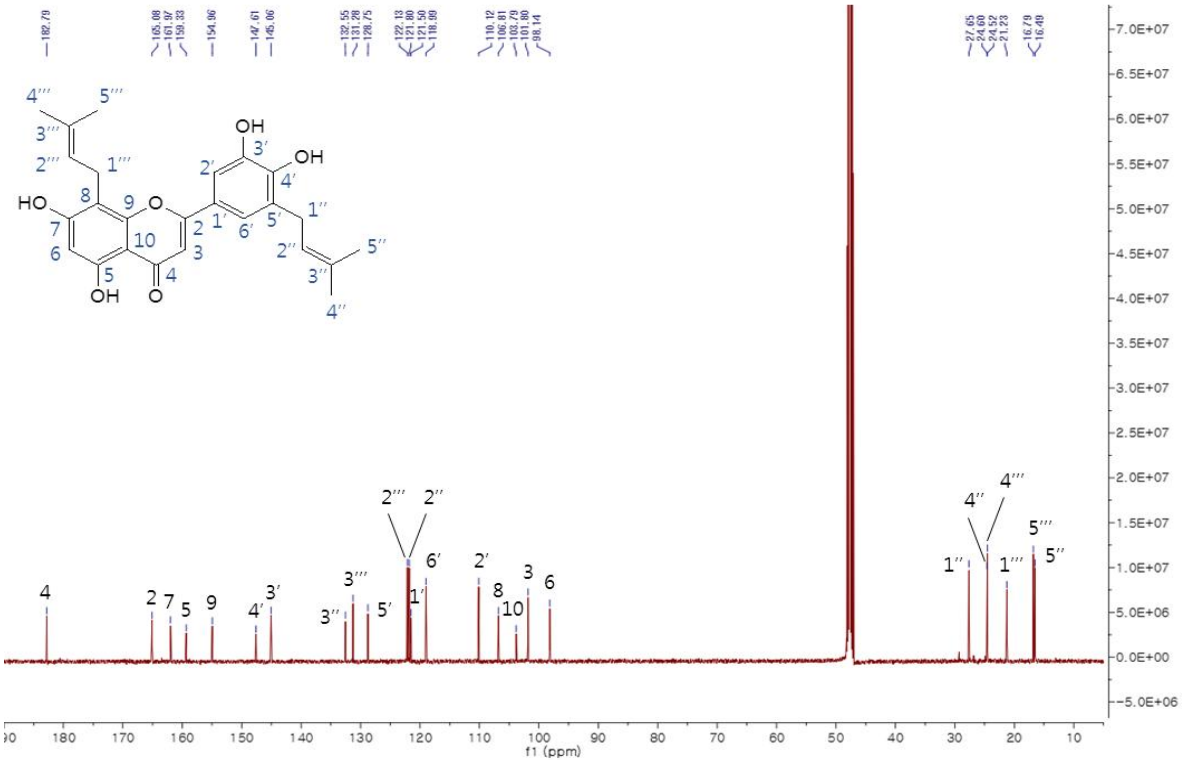
^{1}H NMR

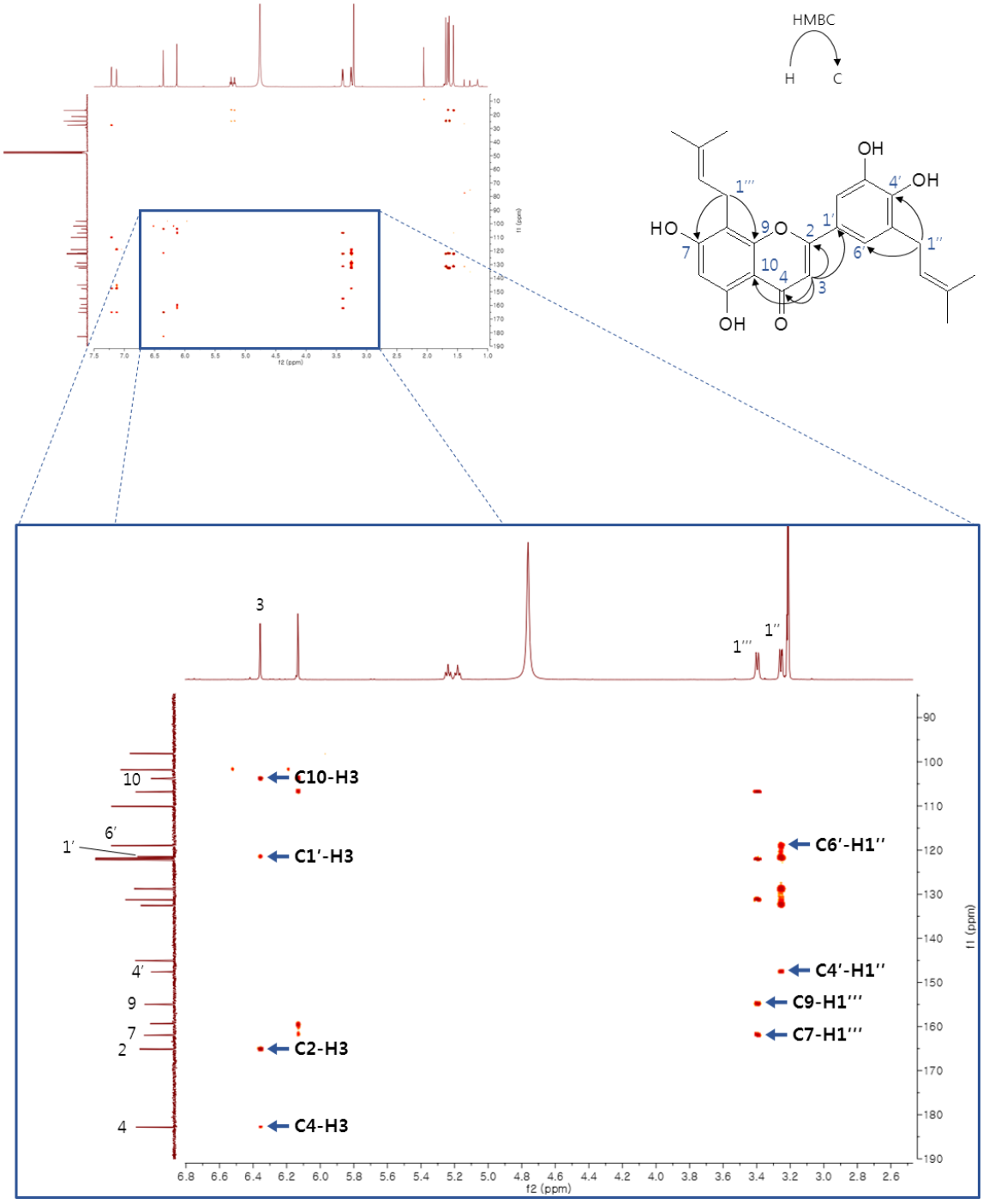


^{13}C NMR

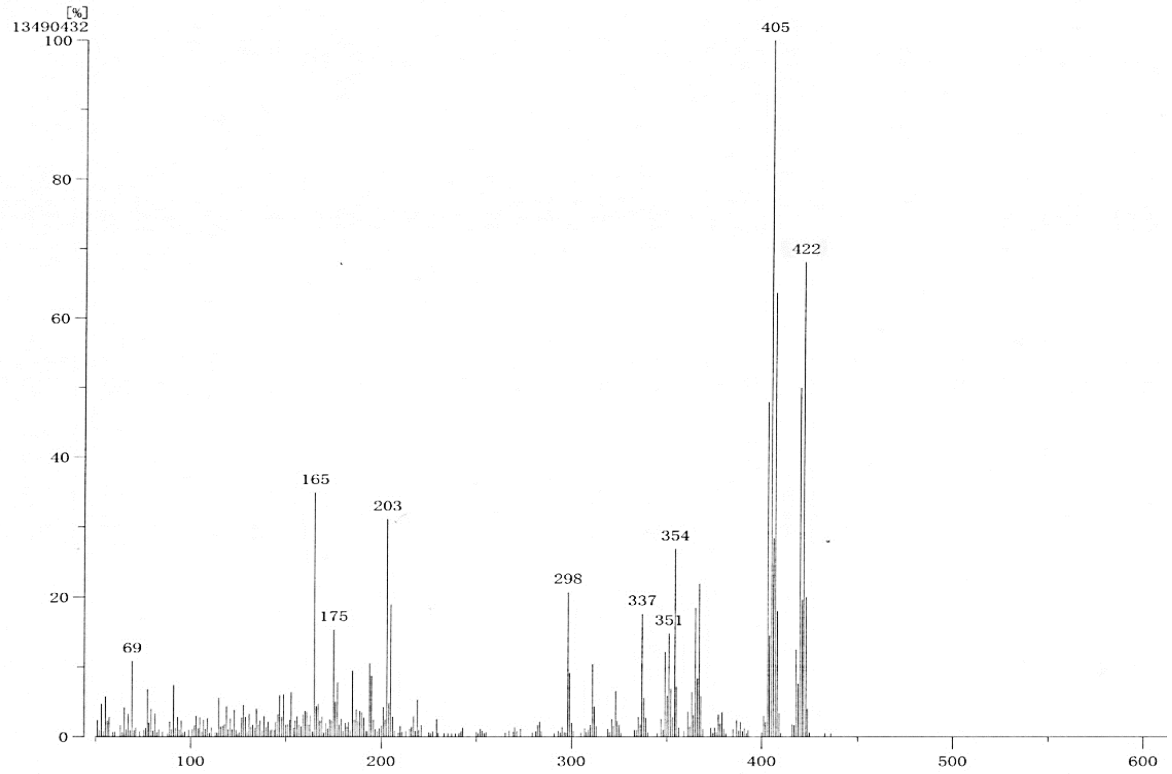


S1: ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz) spectrum of compound **1** (MeOD).

HMBC



S2: HMBC spectrum of compound **1**.



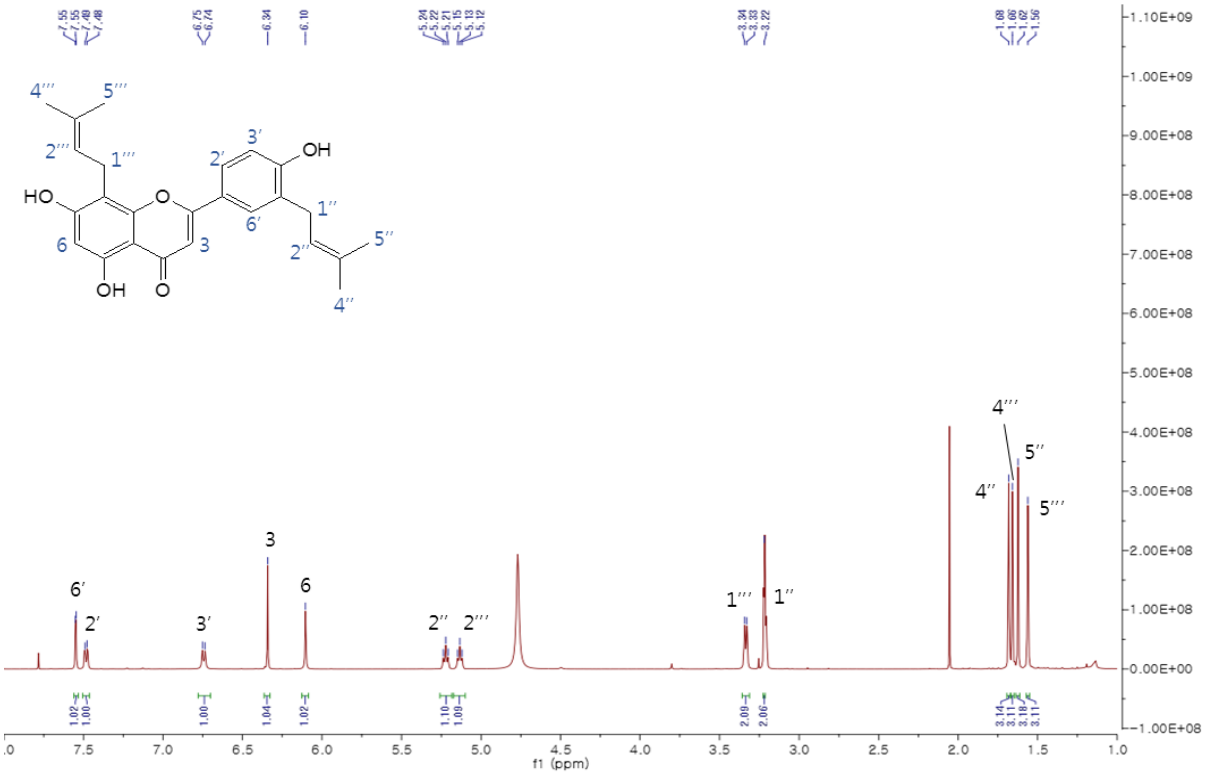
Data : 45-b1-HR Date : 11-Jul-2016 17:22
Instrument : MStation
Sample : -
Note : -
Inlet : Direct Ion Mode : EI+
RT : 0.84 min Scan# : 26
Elements : C 100/1, H 100/1, O 10/1
Mass Tolerance : 1000ppm, 3mmu if m/z > 3
Unsaturation (U.S.) : -0.5 - 20.0

	Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1	422.1727	54.93	-0.6 / -0.2	13.0	C25 H26 O6

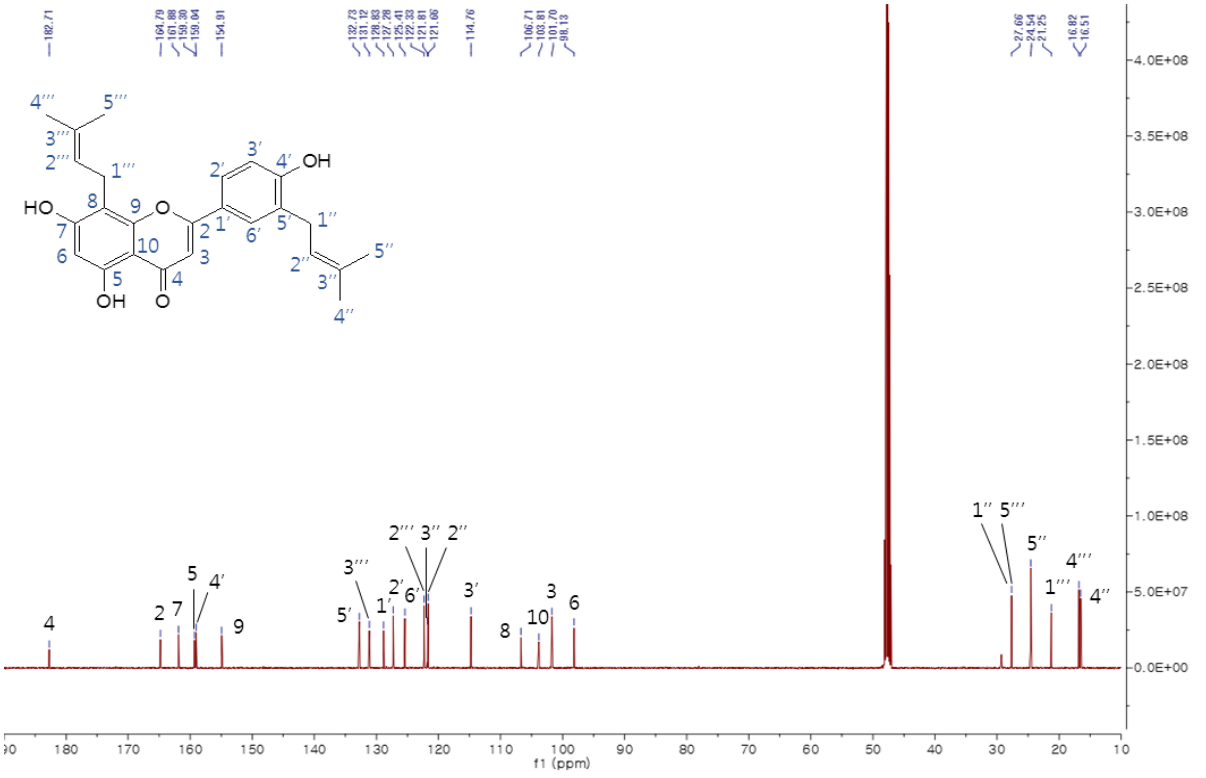
S3: HREIMS data of compound **1**.

Epimedokoreanin B ***(1)****:* pale yellow powder; EIMS, *m/z* 422 $[M]^+$; HREIMS, *m/z* 422.1727 (calcd for $C_{25}H_{26}O_6$); ^{1}H-NMR (MeOD, 500 MHz) δ_H 6.36 (1H, s), 6.13 (1H, s), 7.13 (1H, d, *J* = 2.1 Hz), 7.21 (1H, d, *J* = 2.2 Hz), 3.25 (2H, d, *J* = 7.3 Hz), 5.18 (1H, m), 1.66 (3H, d, *J* = 0.9 Hz), 1.57 (3H, d, *J* = 0.8 Hz), 3.40 (2H, d, *J* = 7.1 Hz), 5.24 (1H, dddd, *J* = 7.4, 6.0, 2.8, 1.4 Hz), 1.69 (3H, s), 1.64 (3H, s). ^{13}C-NMR (MeOD, 500 MHz) δ_C 165.08, 101.80, 182.79, 159.33, 99.14, 161.97, 106.81, 154.96, 103.79, 121.50, 110.12, 145.06, 147.61, 128.75, 118.99, 27.65, 121.80, 132.55, 24.60, 16.49, 21.23, 122.13, 131.28, 24.52, 16.19.

^{1}H NMR

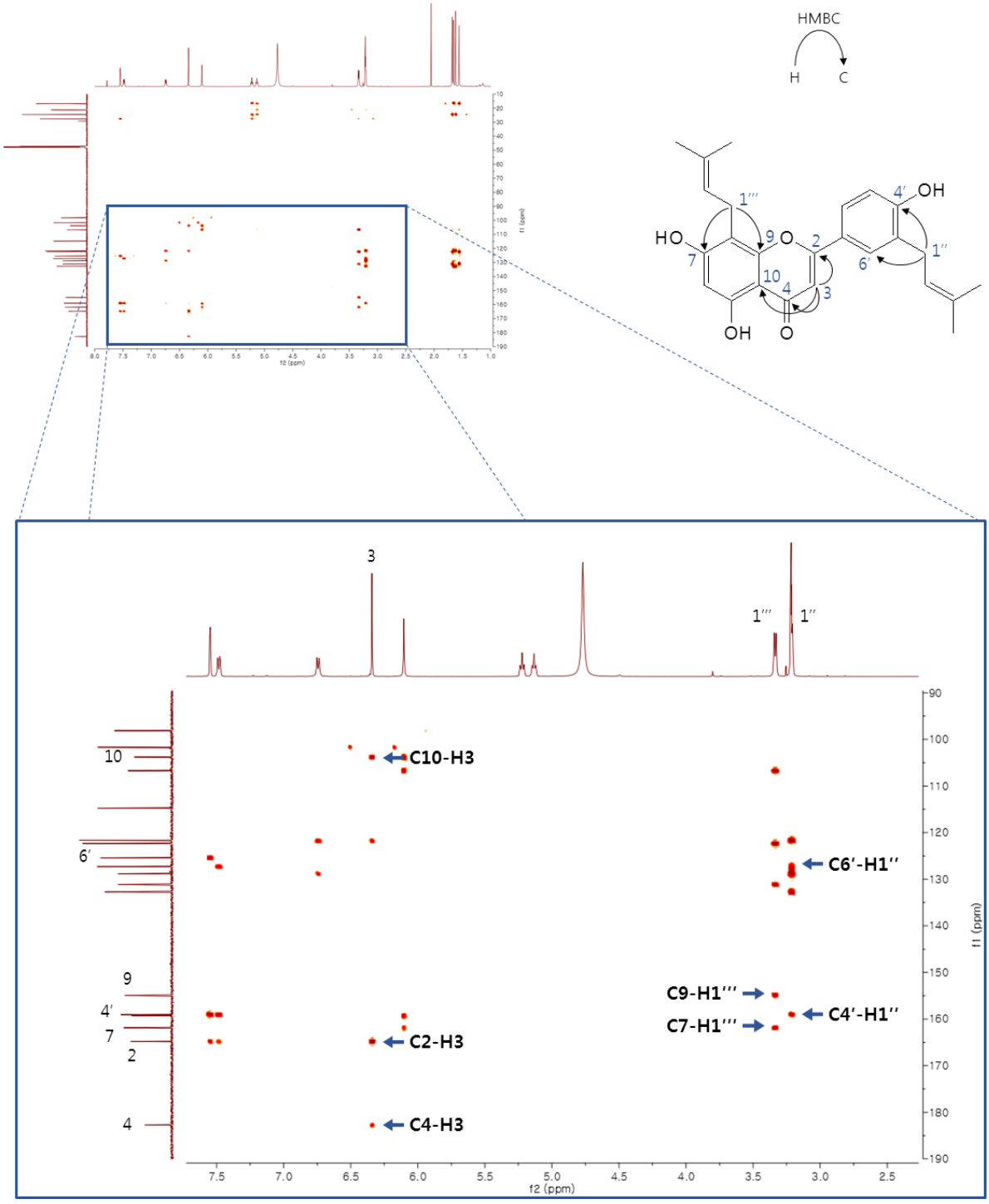


^{13}C NMR

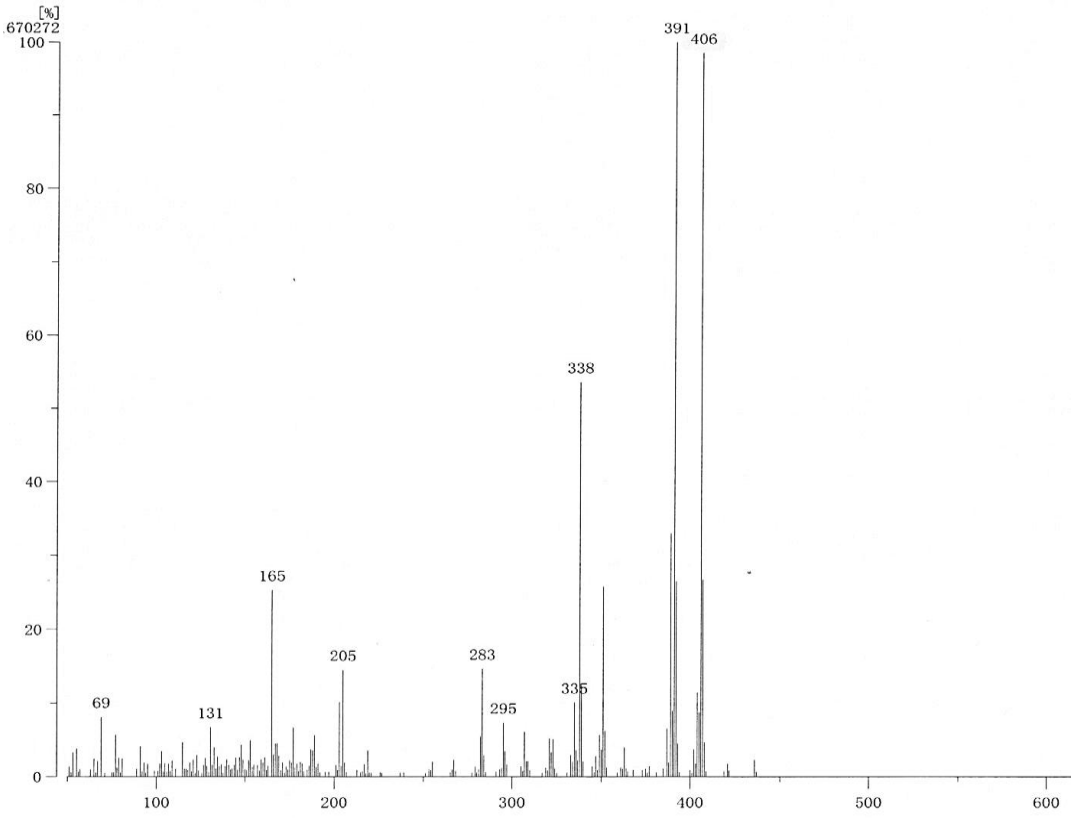


S4: ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz) spectrum of compound **2** (MeOD).

HMBC



S5: HMBC spectrum of compound **2**.



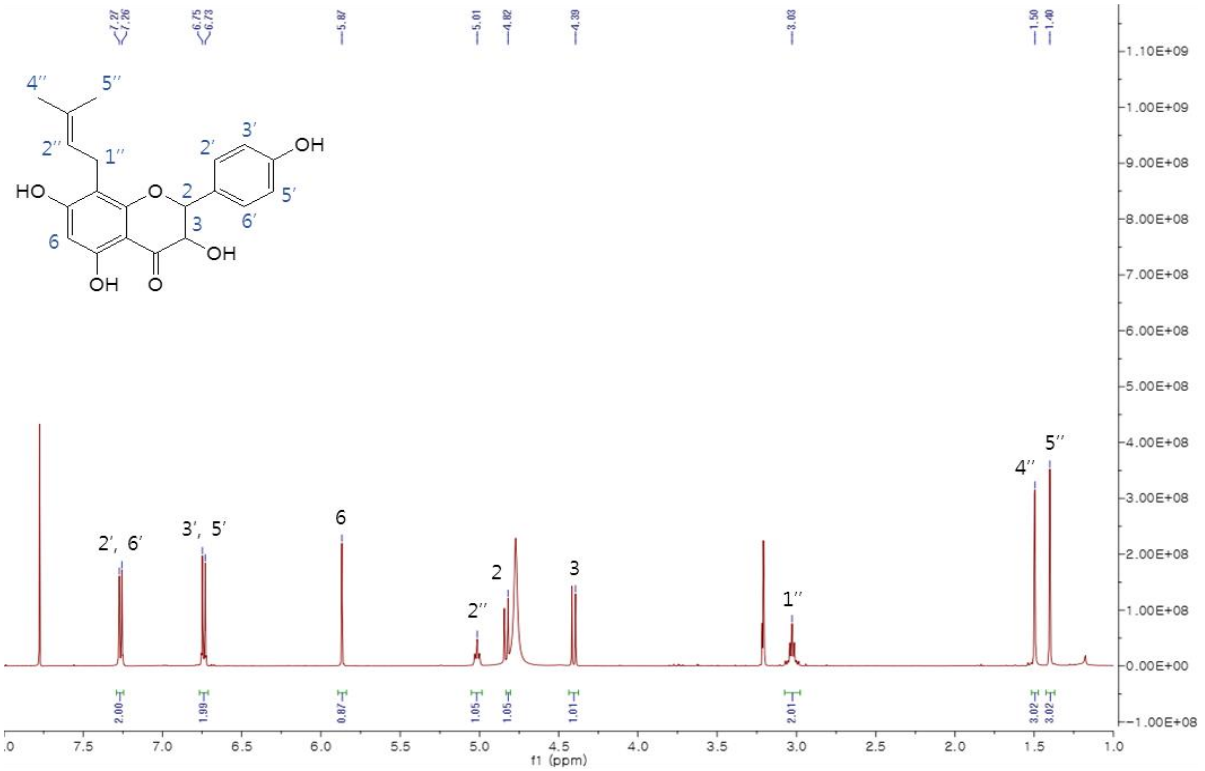
Data : 37_26_1_HR Date : 16-Aug-2016 18:06
Instrument : MStation
Sample : -
Note : -
Inlet : Direct Ion Mode : EI+
RT : 0.87 min Scan# : 27
Elements : C 100/1, H 100/1, O 10/1
Mass Tolerance : 1000ppm, 3mmu if m/z > 3
Unsaturation (U.S.) : -0.5 - 20.0

	Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1	406.1776	100.00	-1.0 / -0.4	13.0	C25 H26 O5

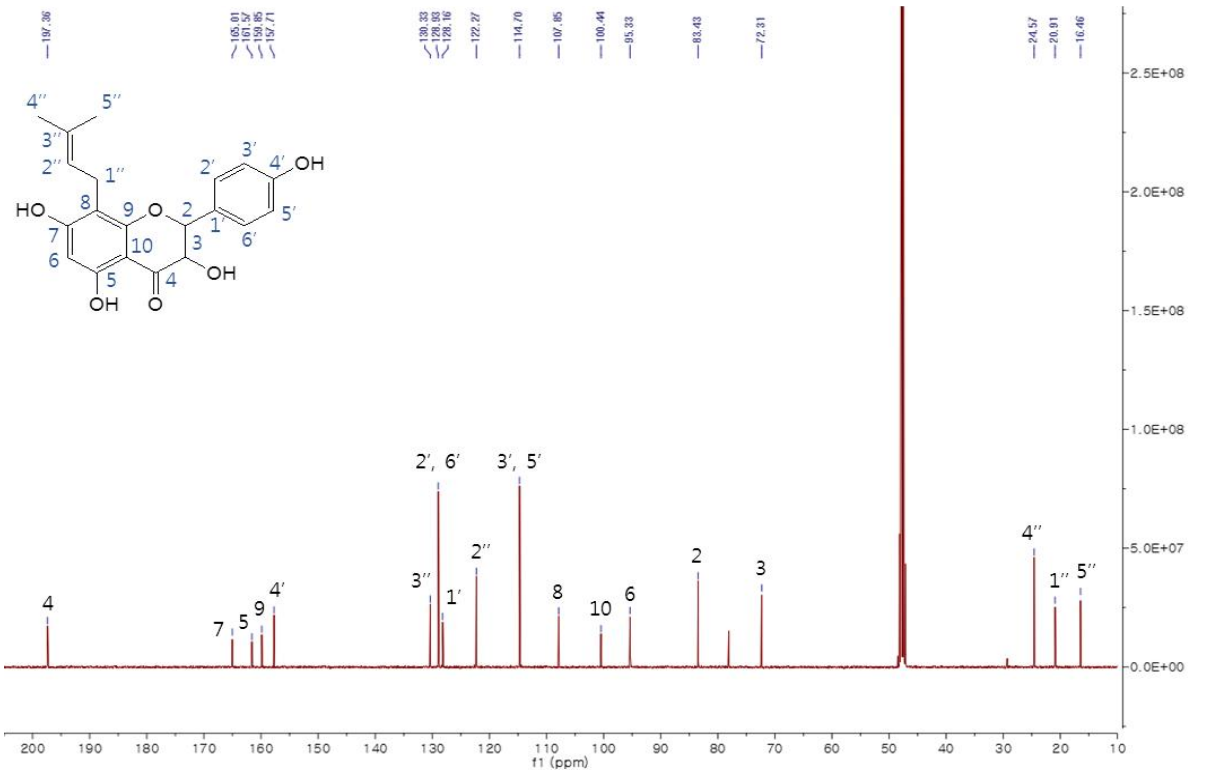
S6: HREIMS data of compound **2**.

*5, 7, 4'-trihydroxy-8, 3'-diprenylflavone (**2**):* white powder; EIMS, *m/z* 406 $[M]^+$; HREIMS, *m/z* 406.1776 (calcd for $C_{25}H_{26}O_5$); ^{1}H-NMR (MeOD, 500 MHz) δ_H 6.34 (1H, s), 6.10 (1H, s), 7.48 (1H, d, *J* = 6.5 Hz), 6.74 (1H, d, *J* = 8.3 Hz), 7.55 (1H, d, *J* = 2.1 Hz), 3.22 (2H, s), 5.22 (1H, t, *J* = 7.4 Hz), 1.68 (3H, s), 1.62 (3H, s), 3.34 (2H, d, *J* = 6.9 Hz), 5.13 (1H, t, *J* = 6.9 Hz), 1.66 (3H, s), 1.56 (3H, s). ^{13}C-NMR (MeOD, 500 MHz) δ_C 164.79, 101.70, 182.71, 159.30, 98.13, 161.88, 106.71, 154.91, 103.81, 128.83, 127.28, 114.76, 159.04, 132.73, 125.41, 29.28, 121.66, 121.81, 16.51, 21.25, 24.54, 122.33, 131.12, 16.82, 27.66.

^{1}H NMR

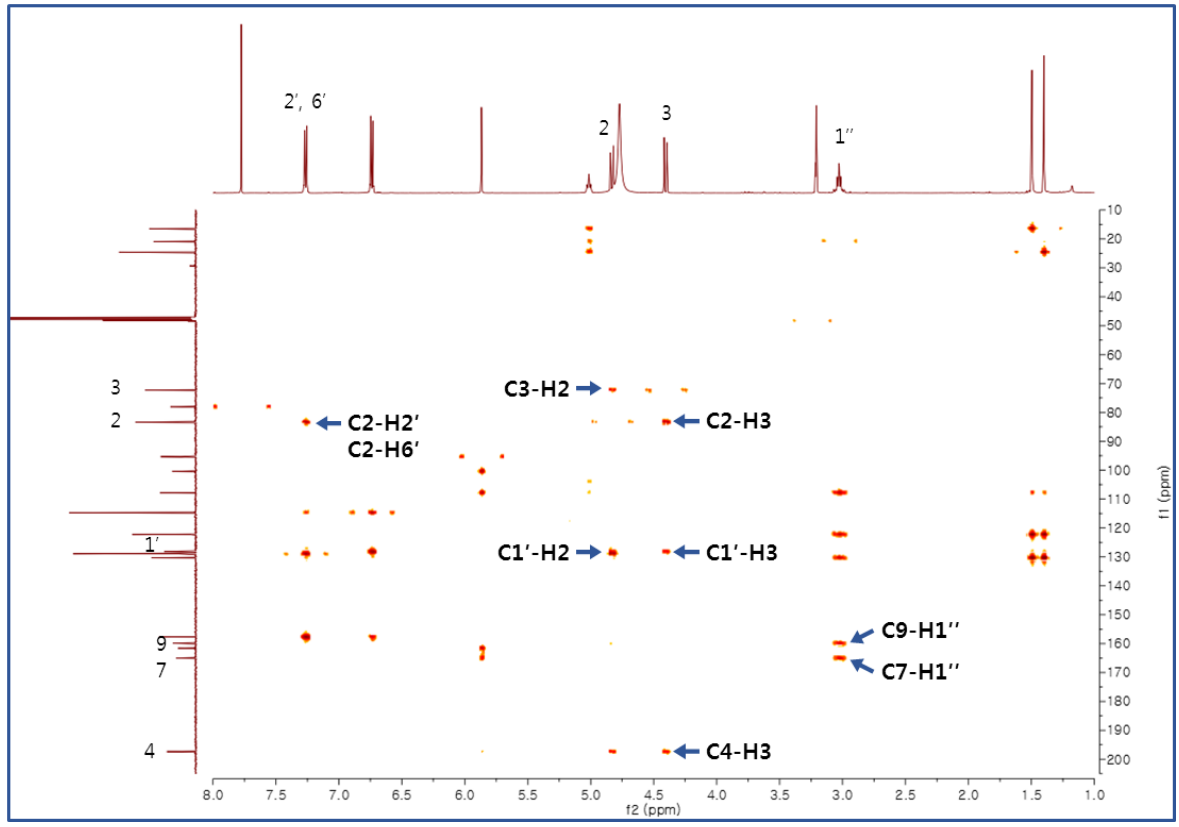


^{13}C NMR

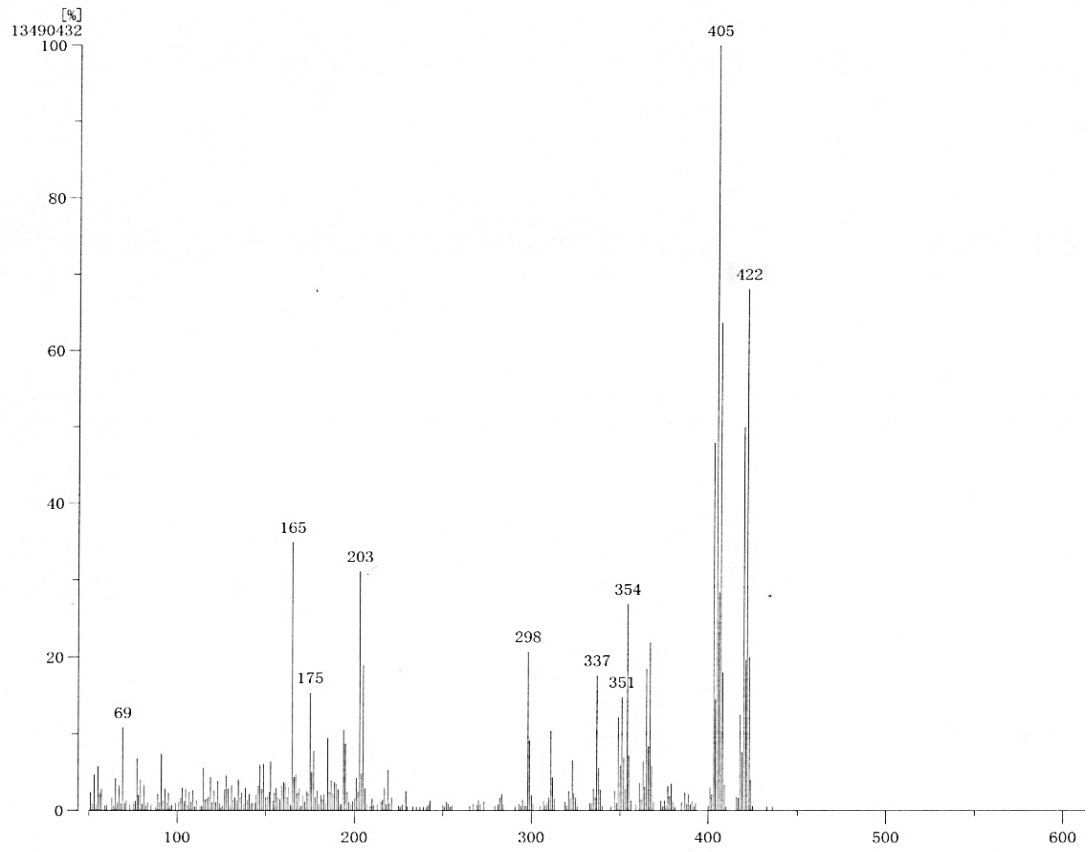


S7: ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz) spectrum of compound **3** (MeOD).

HMBC



S8: HMBC spectrum of compound **3**.



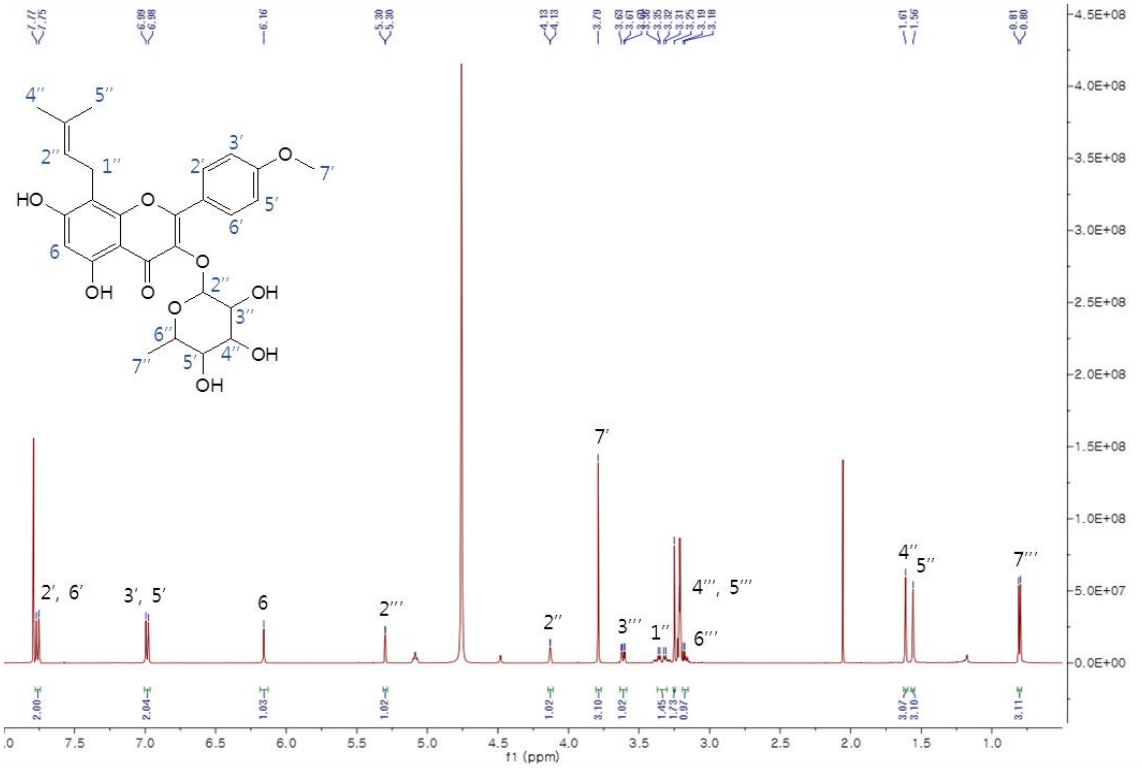
Data : 45-b1-HR Date : 11-Jul-2016 17:22
Instrument : MStation
Sample : -
Note : -
Inlet : Direct Ion Mode : EI+
RT : 0.84 min Scan# : 26
Elements : C 100/1, H 100/1, O 10/1
Mass Tolerance : 1000ppm, 3mmu if m/z > 3
Unsaturation (U.S.) : -0.5 - 20.0

	Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1	422.1727	54.93	-0.6 / -0.2	13.0	C25 H26 O6

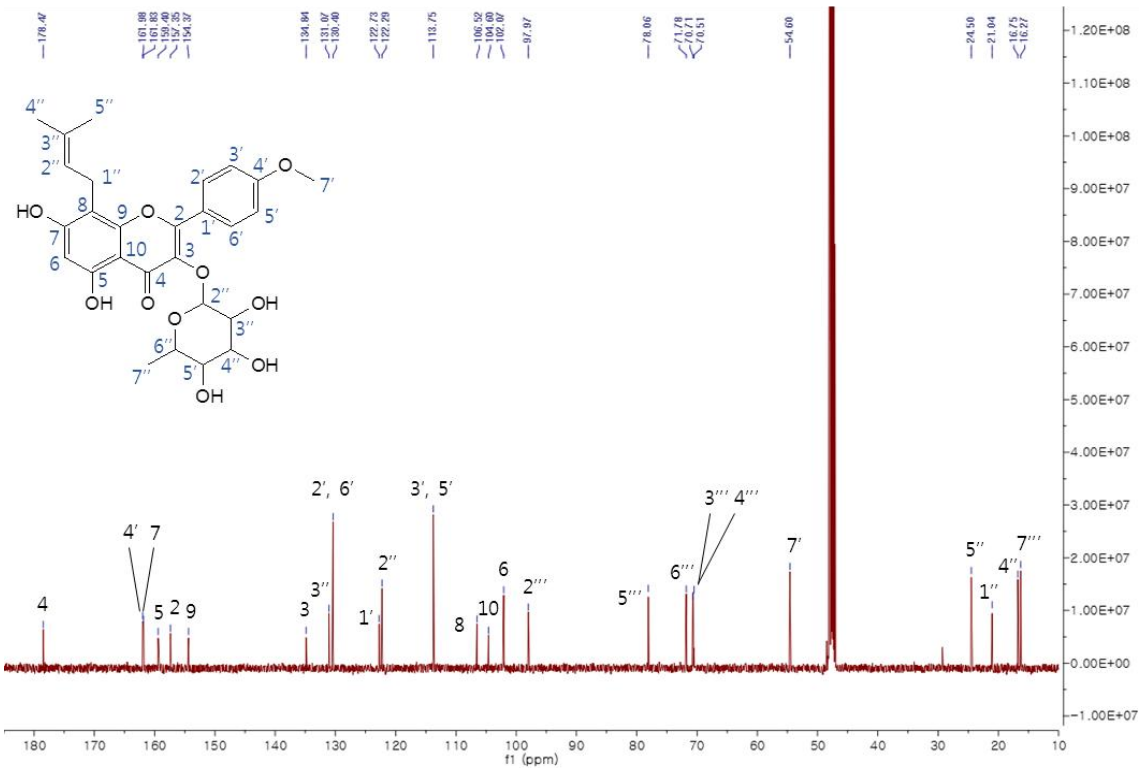
S9: HREIMS data of compound **3**.

*Neophellamuretin (**3**):* yellow powder; EIMS, *m/z* 356 $[M]^+$; HREIMS, *m/z* 356.1260 (calcd for $C_{20}H_{20}O_6$); ^{1}H-NMR (MeOD, 500 MHz) δ_H 4.82 (1H, s), 4.39 (1H, s), 8.87 (1H, s), 7.26 (2H, d, J = 8.5 Hz), 6.74 (2H, d, J = 8.6 Hz), 3.03 (2H, s), 5.01 (1H, s), 1.50 (3H, s), 1.40 (3H, s). ^{13}C-NMR (MeOD, 500 MHz) δ_C 83.43, 72.31, 197.36, 161.57, 95.33, 165.01, 107.85, 159.85, 100.44, 128.16, 128.93, 114.70, 157.71, 20.91, 122.27, 130.33, 24.57, 16.46.

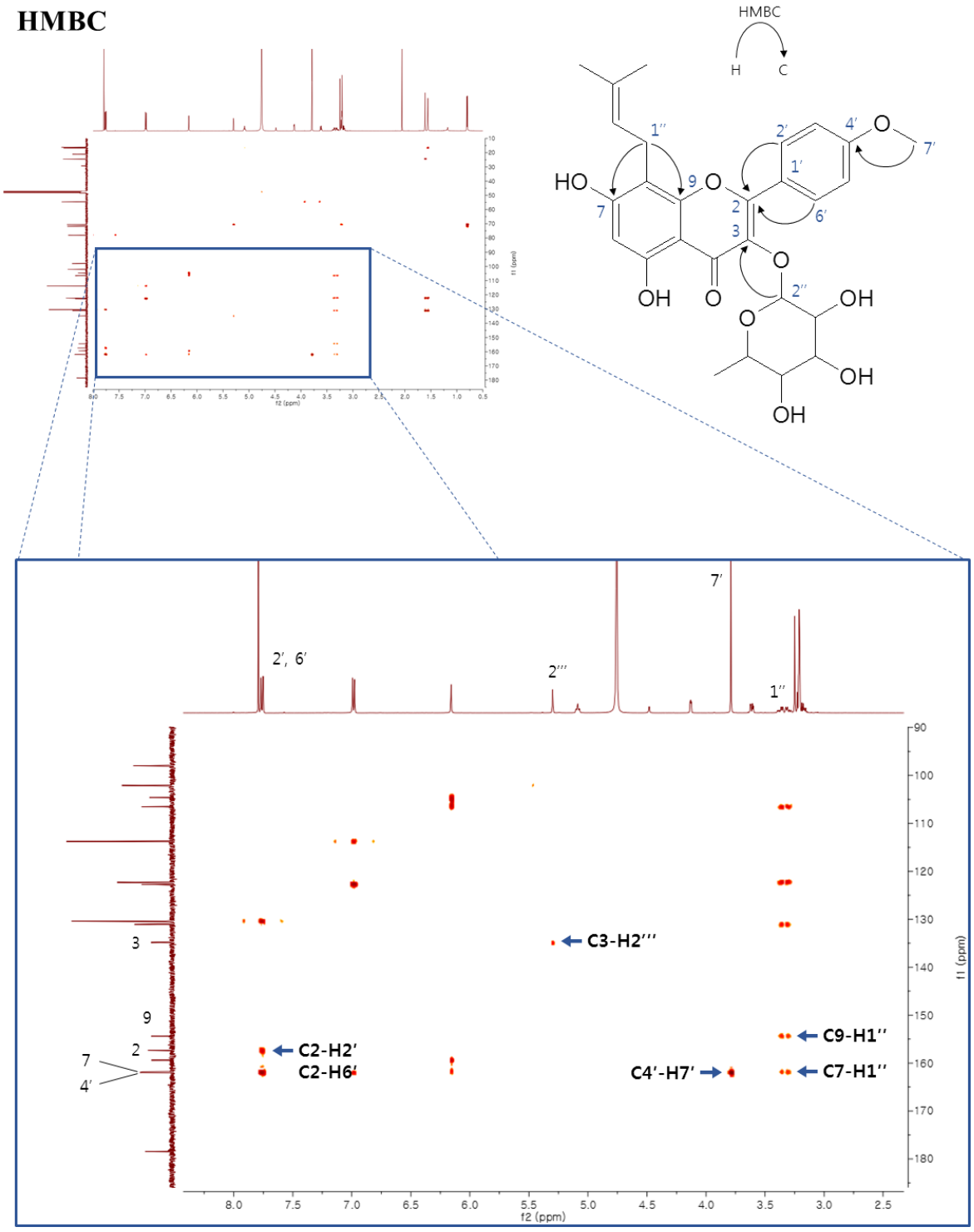
^{1}H NMR



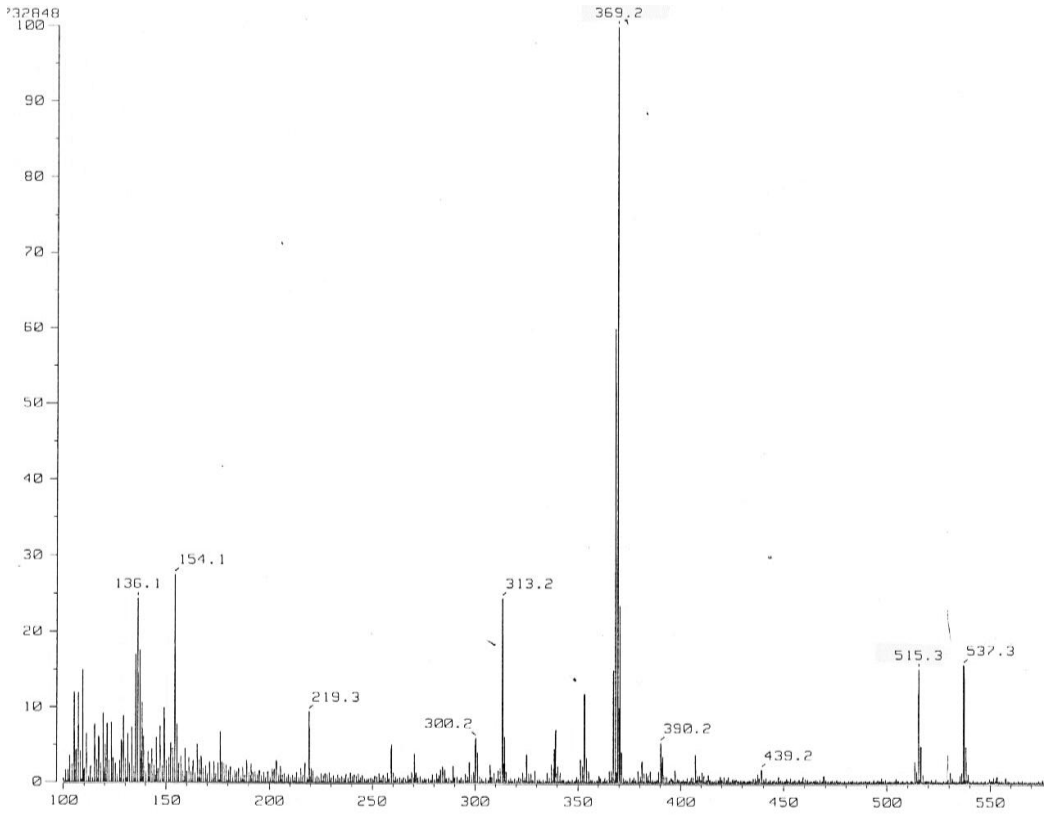
^{13}C NMR



S10: ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz) spectrum of compound **4** (MeOD).



S11: HMBC spectrum of compound **4**.

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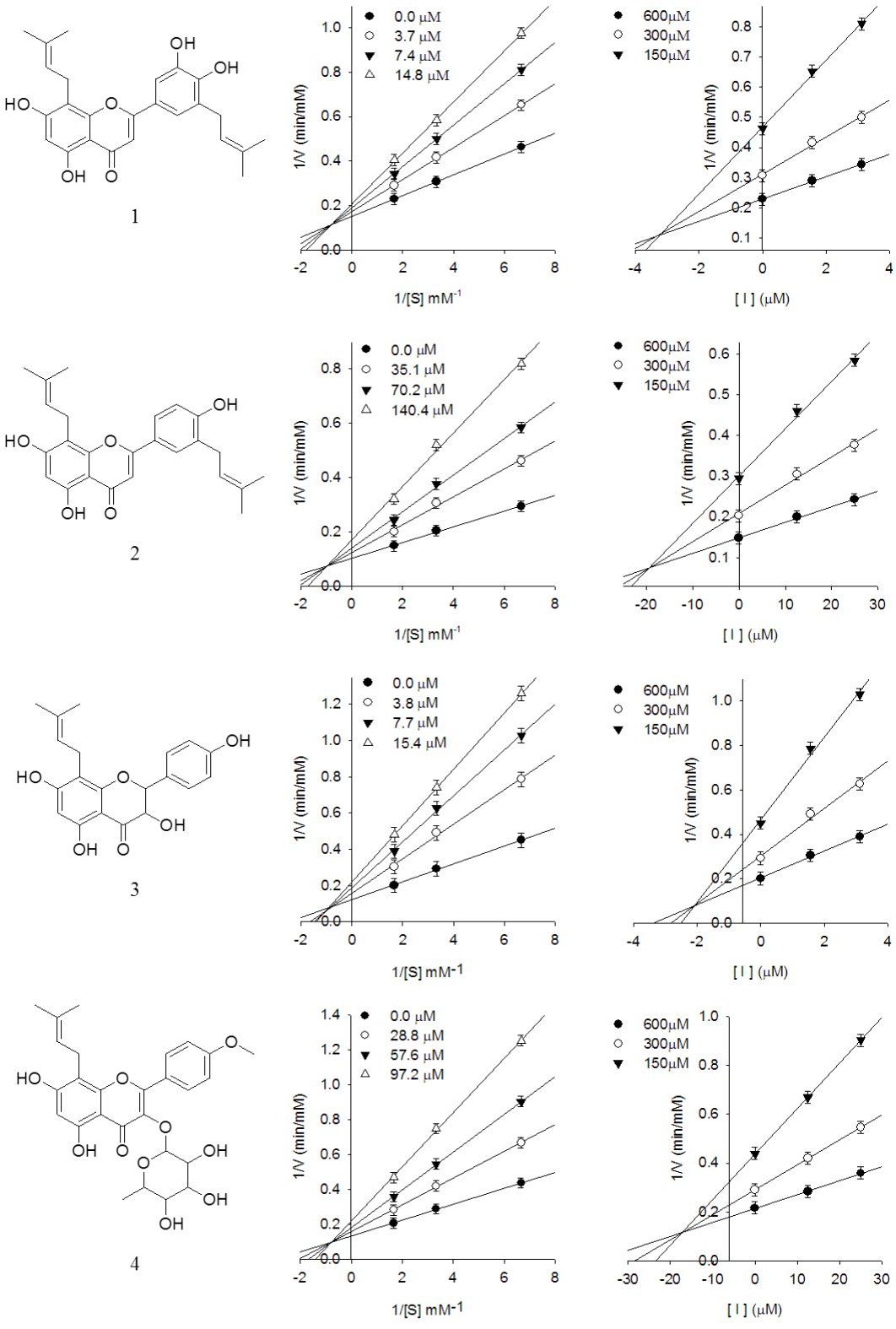
[ Elemental Composition ]
Data  : 65-b2-HR                        Date : 11-Oct-2016 15:14
Sample: -
Note : -
Inlet : Direct                          Ion Mode : FAB+
RT : 1.92 min                           Scan#: 24
Elements : C 100/1, H 150/1, O 10/1
Mass Tolerance      : 100ppm, 3mmu if m/z > 30
Unsaturation (U.S.) : 0.0 - 20.0

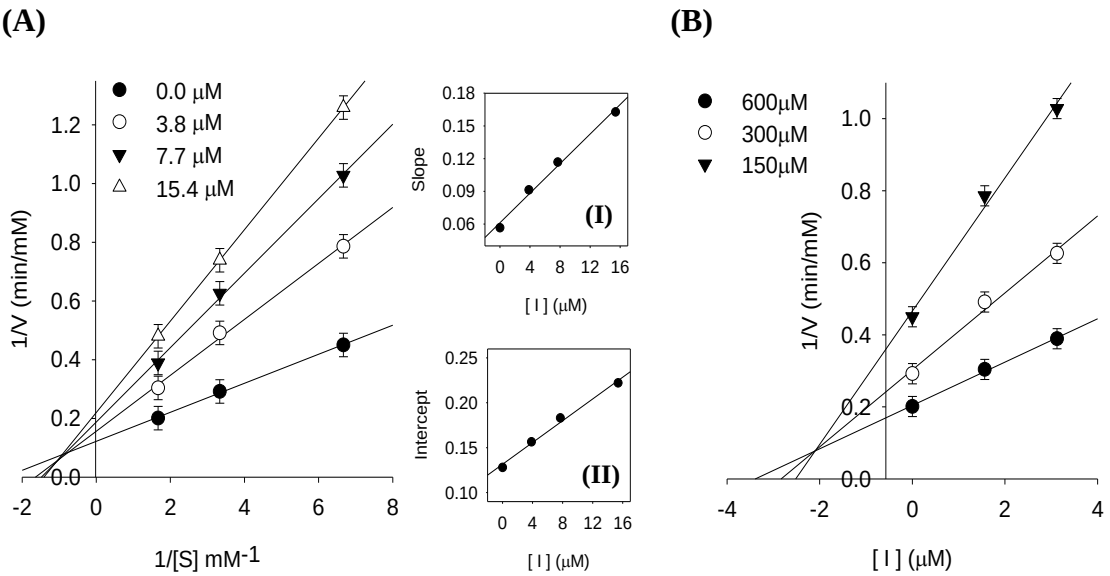
Observed m/z Int%   Err[ppm / mmu]    U.S.  Composition
  369.1329   100.0     -2.4 /  -0.9   11.5  C 21 H 21 O 6
```

S12: HRFABMS data of compound **4**.

*Icariside II (**4**):* pale yellow powder; EIMS, *m/z* 369 $[M]^+$; HRFABMS, *m/z* 369.1329 (calcd for $C_{21}H_{21}O_6$); ^{1}H-NMR (MeOD, 500 MHz) δ_H 6.16 (1H, s), 7.76 (2H, d, *J* = 9.0 Hz), 6.99 (2H, d, *J* = 9.0 Hz), 3.79 (3H, s), 3.34 (2H, dd, *J* = 20.5, 6.8 Hz), 4.13 (1H, d, *J* = 1.6 Hz), 1.61 (3H, s), 1.56 (3H, s), 5.30 (1H, d, *J* = 1.5 Hz), 3.61 (1H, dd, *J* = 9.2, 3.3 Hz), 3.25 (2H, s), 3.25 (2H, s), 3.18 (1H, d, *J* = 6.0 Hz), 0.80 (3H, d, *J* = 6.0 Hz). ^{13}C-NMR (MeOD, 500 MHz) δ_C 157.35, 134.84, 178.47, 159.40, 102.07, 161.83, 106.52, 154.37, 104.60, 122.73, 130.40, 113.75, 161.98, 54.60, 21.04, 122.29, 131.07, 16.75, 24.50, 97.97, 70.71, 70.51, 78.06, 71.78, 16.27.



S13: Lineweaver-Burk plot for the inhibition of human neutrophil elastase by compound **1**-**4** (left). Dixon plots for the inhibition of compound **1**-**4** (right).



S14: (A) Lineweaver-Burk plot were constructed for the inhibition of HNE by compounds **2**. Insets (I) and (II) represent secondary plot of slope and intercept of the straight lines versus concentration of compounds **2**, respectively. (B) Dixon plots for the inhibition of compound **2** on HNE activity.

[Plant Material]

S15: Plant Material

***Epimedium koreanum* NAKAI. (三枝九葉草, 淫羊藿) (삼지구엽초, 음양곽)**

Manufacturer : Handsherb Co.,Ltd, Republic of Korea

752, Cheonmun-ro, Yeongcheon-si, Gyeongsangbuk-do, Republic of Korea