

# SUPPLEMENTARY MATERIALS

## Inhibition of protein tyrosine phosphatase (PTP1B) and $\alpha$ -glucosidase by geranylated flavonoids from *Paulownia tomentosa*

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### ■ Characterization Data

S2-4 : NMR and HREIMS data of compound **1**

S5-7 : NMR and HREIMS data of compound **8**

S8-19 : NMR and HREIMS data of compounds **2-7**

**S20-23 : Isolated compound NMR assign data (<sup>1</sup>H, <sup>13</sup>C)**

S24 : CD spectrum of compounds **1-8**

S25-26 : Enzyme kinetic data of PTP1B

S27-28 : Enzyme kinetic data of  $\alpha$ -glucosidase

S29 : Mixed type parameter of PTP1B ( $K_I, K_{IS}$ )

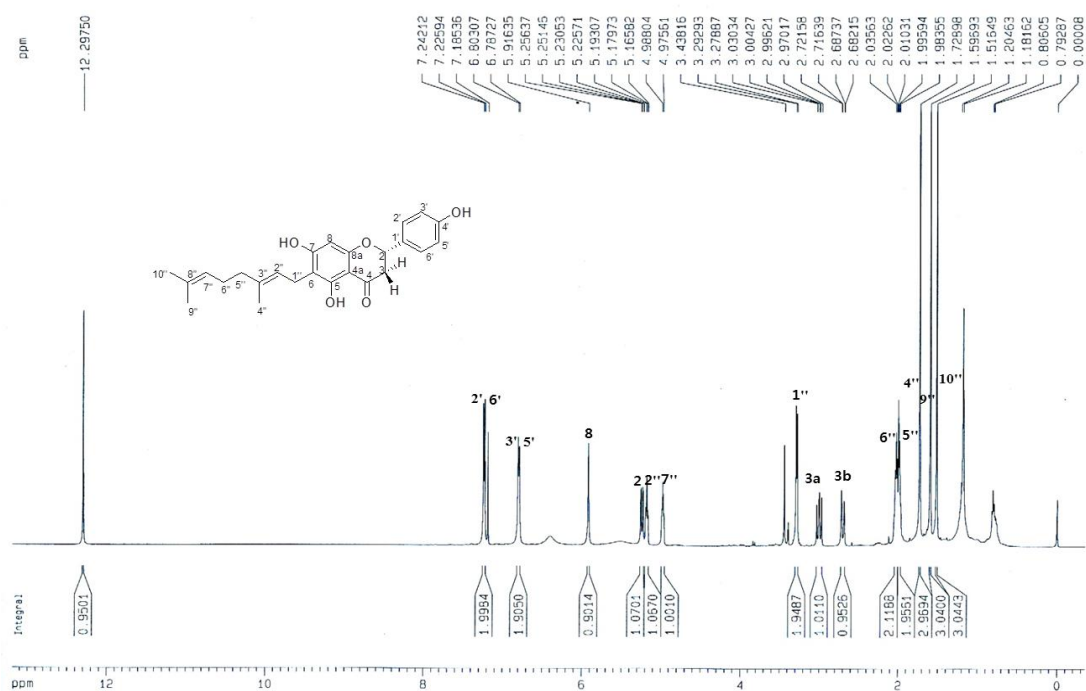


Figure 1.  $^1\text{H-NMR}$  spectrum of compound 1 (500MHz,  $\text{CDCl}_3$ ).

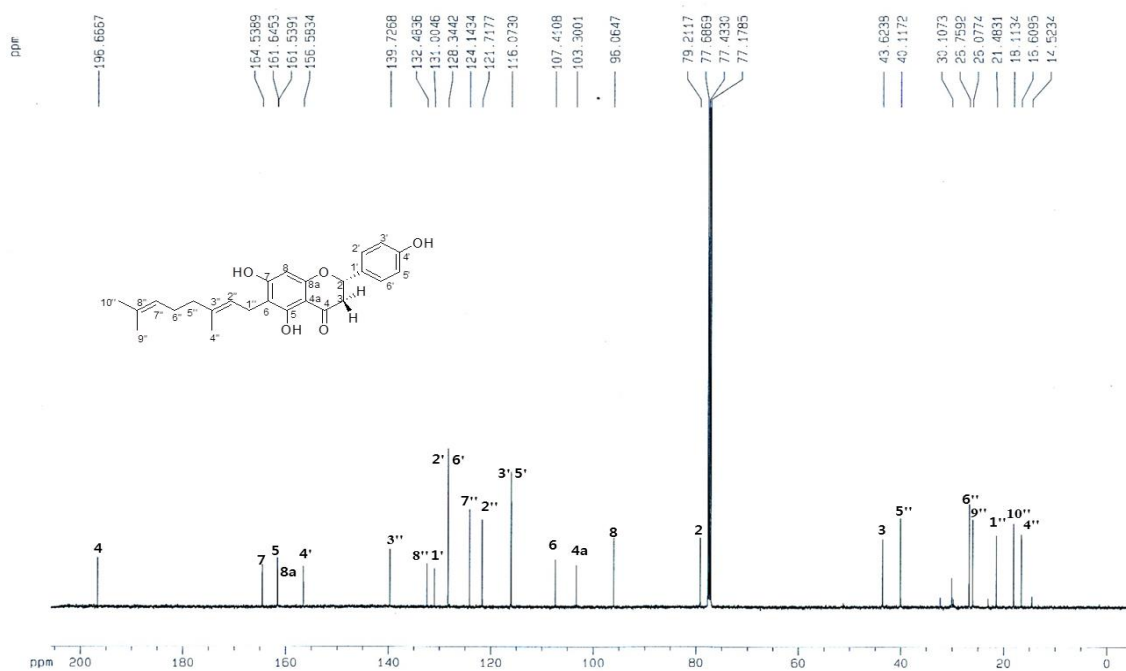


Figure 2.  $^{13}\text{C-NMR}$  spectrum of compound 1 (125MHz,  $\text{CDCl}_3$ ).

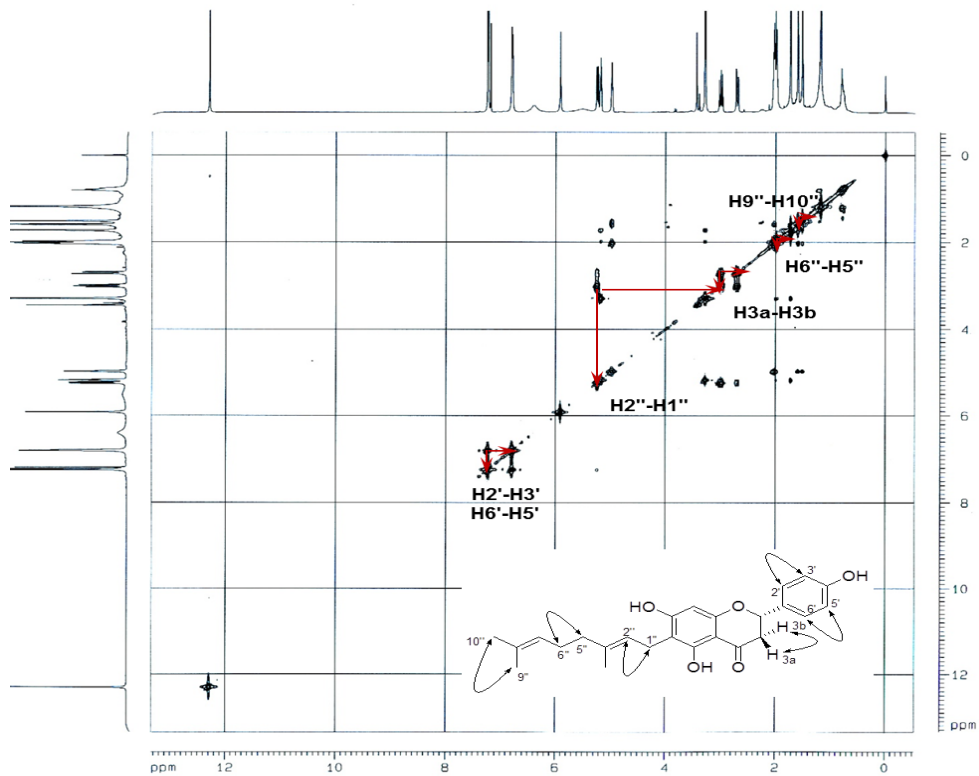


Figure 3.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound **1**.

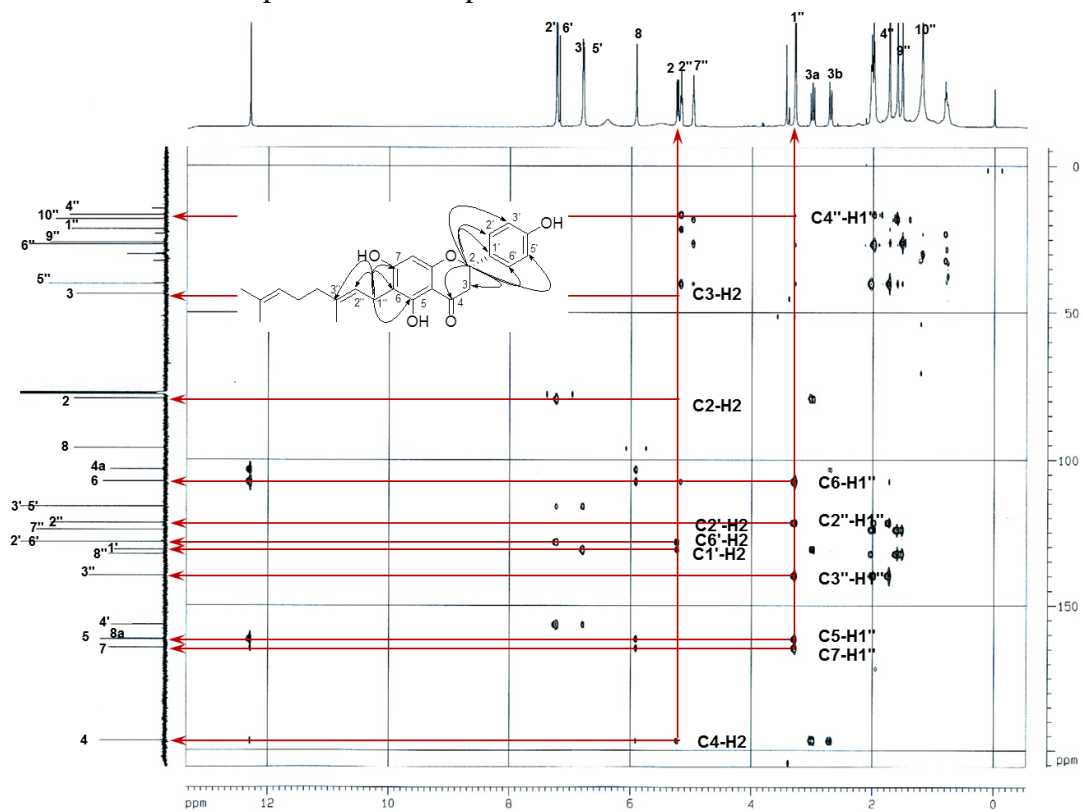


Figure 4. HMBC spectrum of compound **1**.

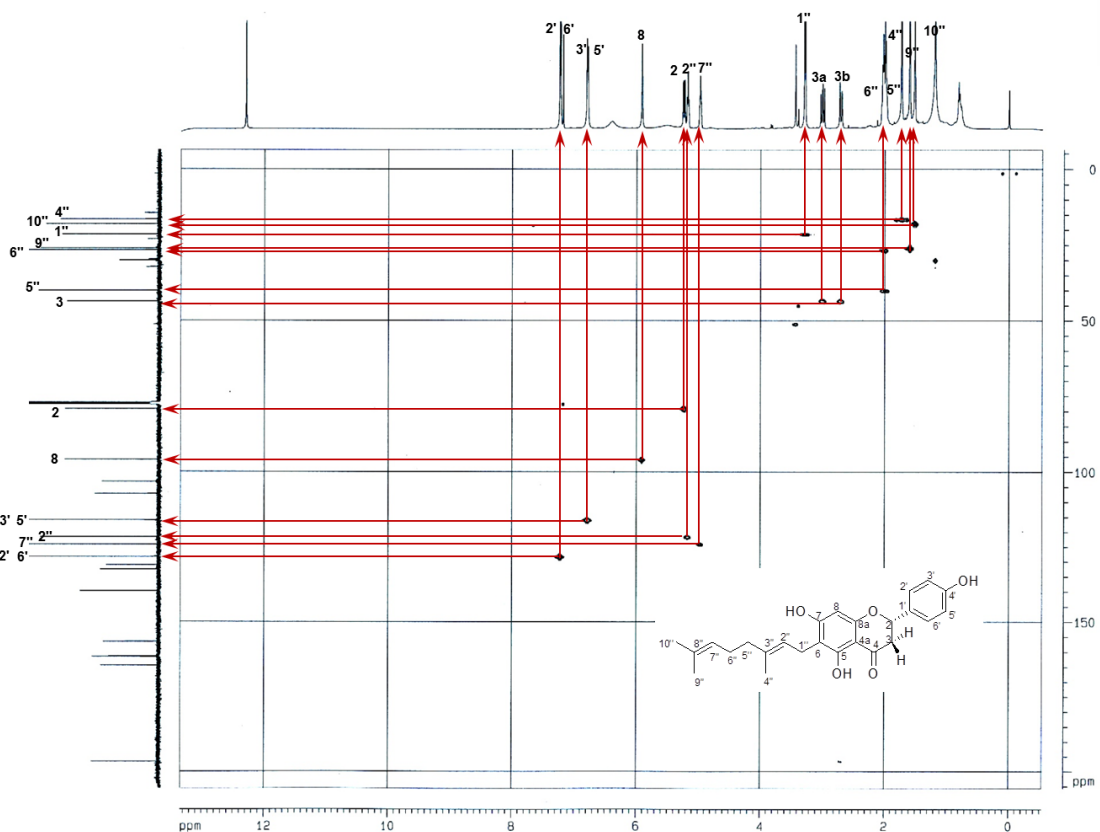
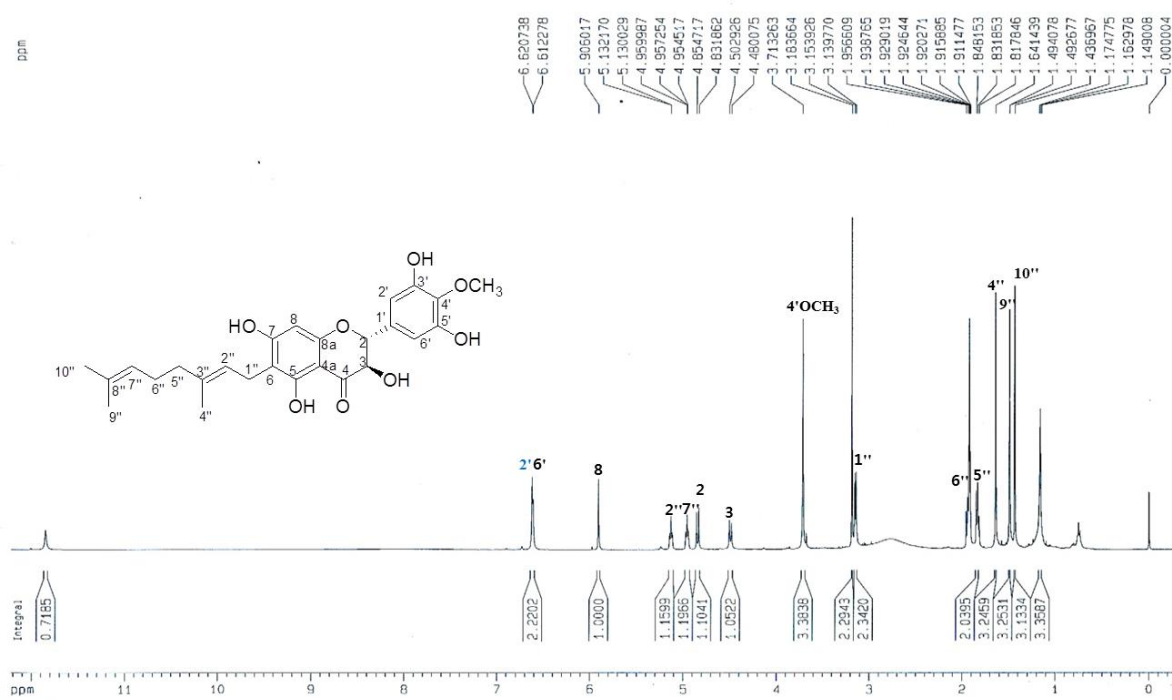


Figure 5. HMQC spectrum of compound 1.

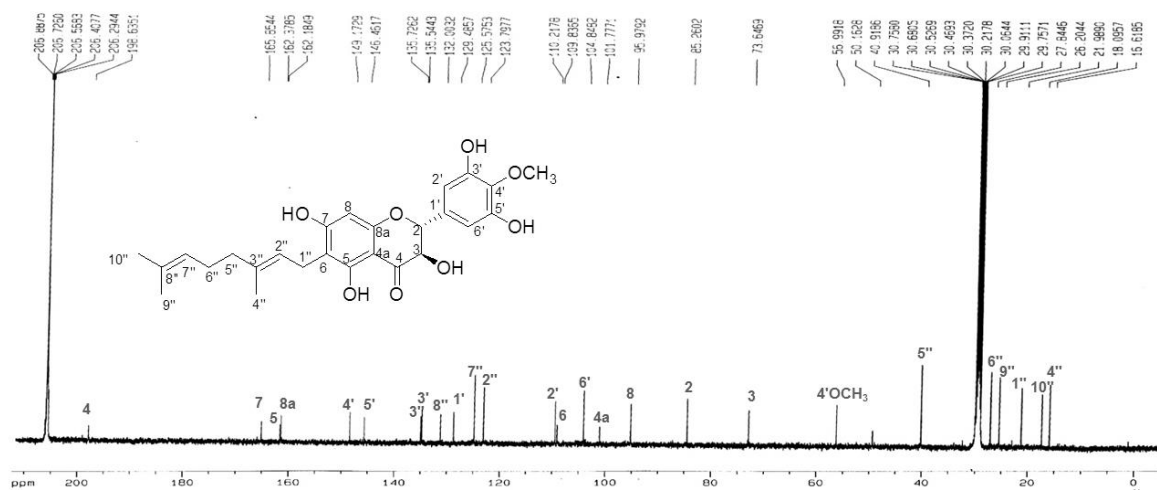
```
[ Elemental Composition ]
Data :
Sample: -
Note : -
Inlet : Direct
RT : 1.95 min
Elements : C 100/1, H 100/0, O 20/1
Mass Tolerance : 1000ppm, 3mmu if m/z < 3, 5mmu if m/z > 5
Unsaturation (U.S.) : 3.0 - 30.0
Ion Mode : EI+
Scan#: 40
```

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
408.1938	100.0	+0.1 / +0.0	3.0	C 25 H 28 O 5

Figure 6. HREIMS data of compound 1.



**Figure 7.** <sup>1</sup>H-NMR spectrum of compound **8** (500MHz, Aceton-d<sub>6</sub>).



**Figure 8.** <sup>13</sup>C-NMR spectrum of compound **8** (125MHz, Aceton-d<sub>6</sub>).

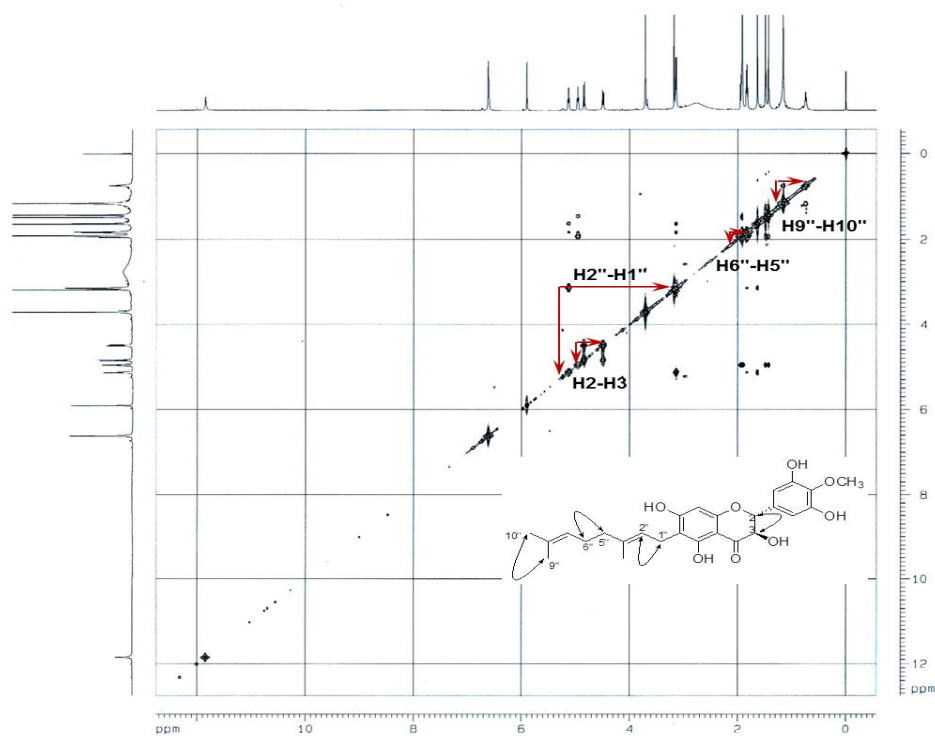


Figure 9. <sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound 8.

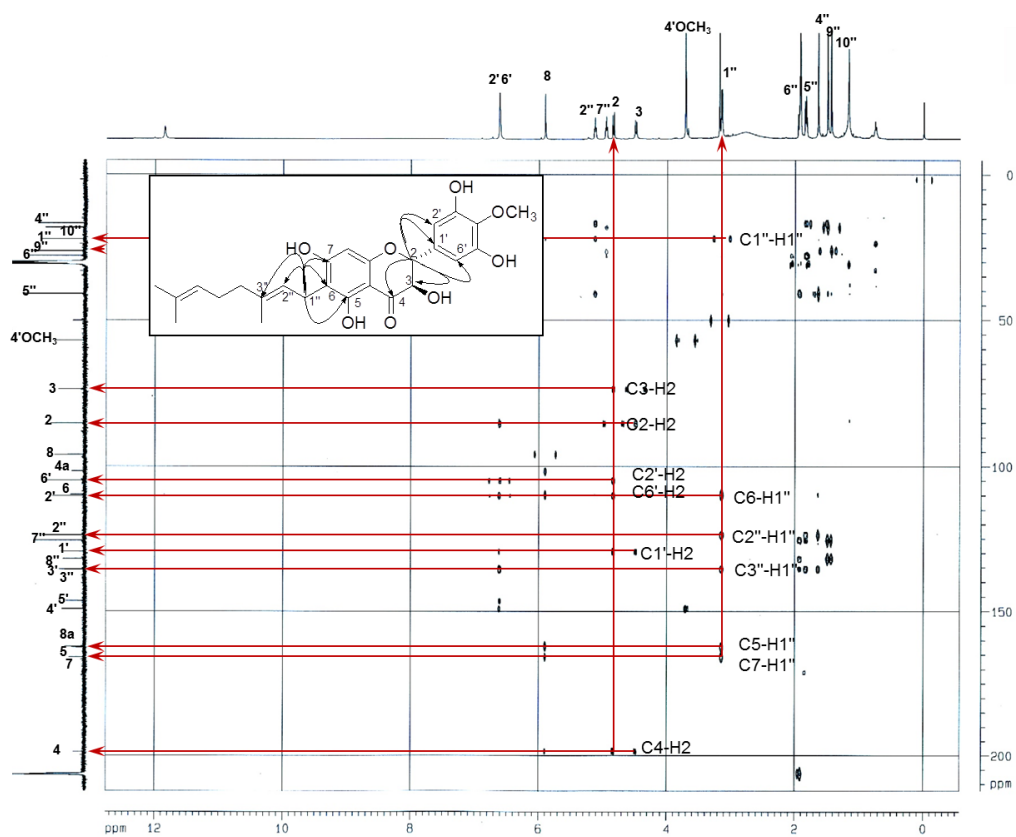


Figure 10. HMBC spectrum of compound 8.

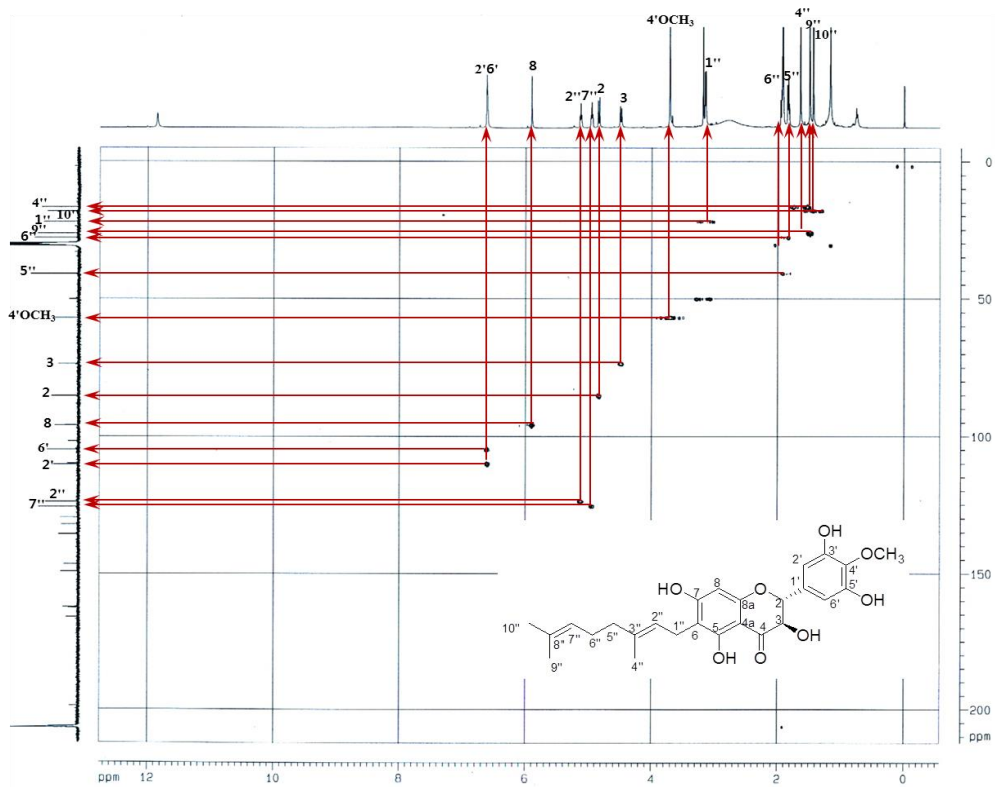


Figure 11. HMOC spectrum of compound 8.

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[ Elemental Composition ]
Data :
Sample: -
Note : -
Inlet : Direct
RT : 2.20 min
Elements : C 100/1, H 100/1, O 20/1
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 10mmu if m/z > 10
Unsaturation (U.S.) : 1.0 - 30.0
Ion Mode : EI+
Scan#: 45
```

Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
470.1943	100.0	+13.0 / +6.1	21.0 C 33 H 26 O 3
		+0.5 / +0.2	12.0 C 26 H 30 O 8
		-12.0 / -5.6	3.0 C 19 H 34 O 13

Figure 12. HREIMS data of compound 8.



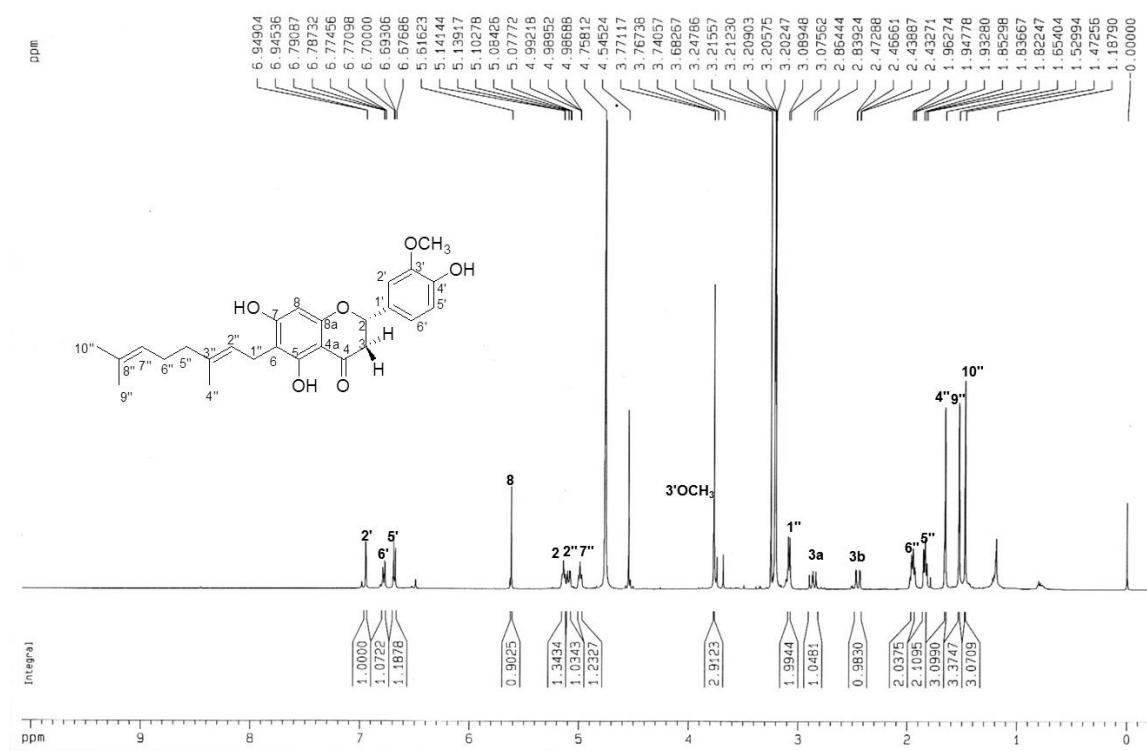


Figure 13.  $^1\text{H-NMR}$  spectrum of compound **2** (500MHz,  $\text{CD}_3\text{OD}$ ).

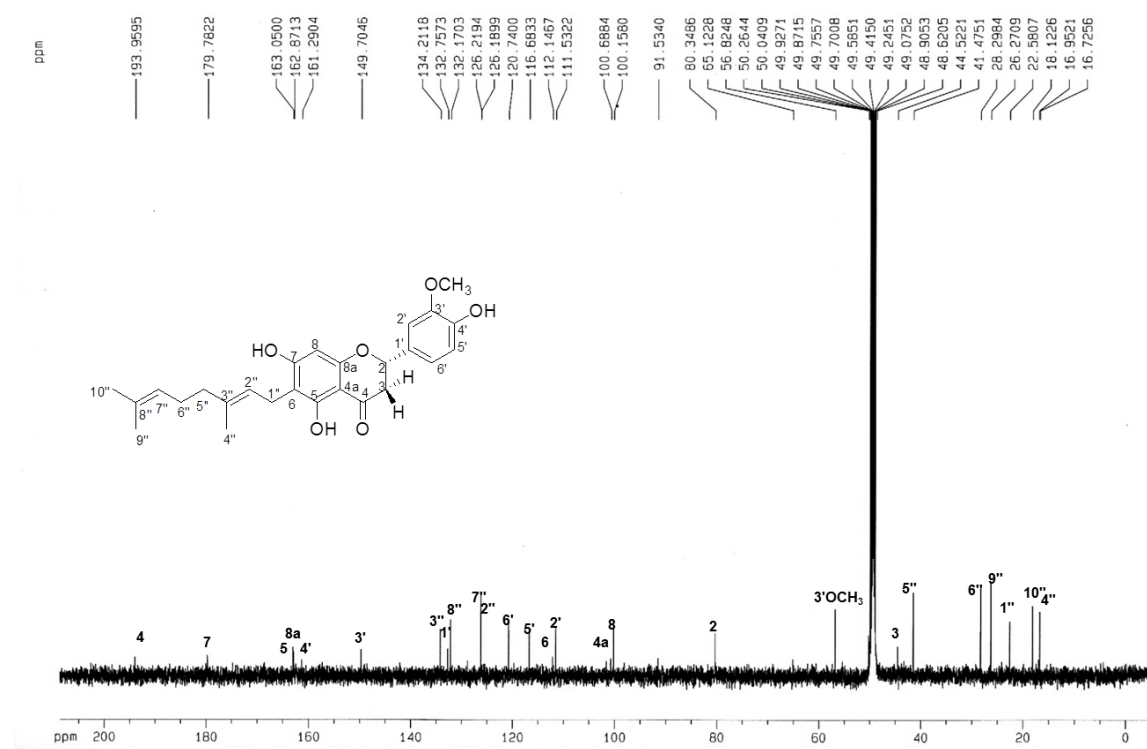


Figure 14.  $^{13}\text{C-NMR}$  spectrum of compound **2** (125MHz,  $\text{CD}_3\text{OD}$ ).



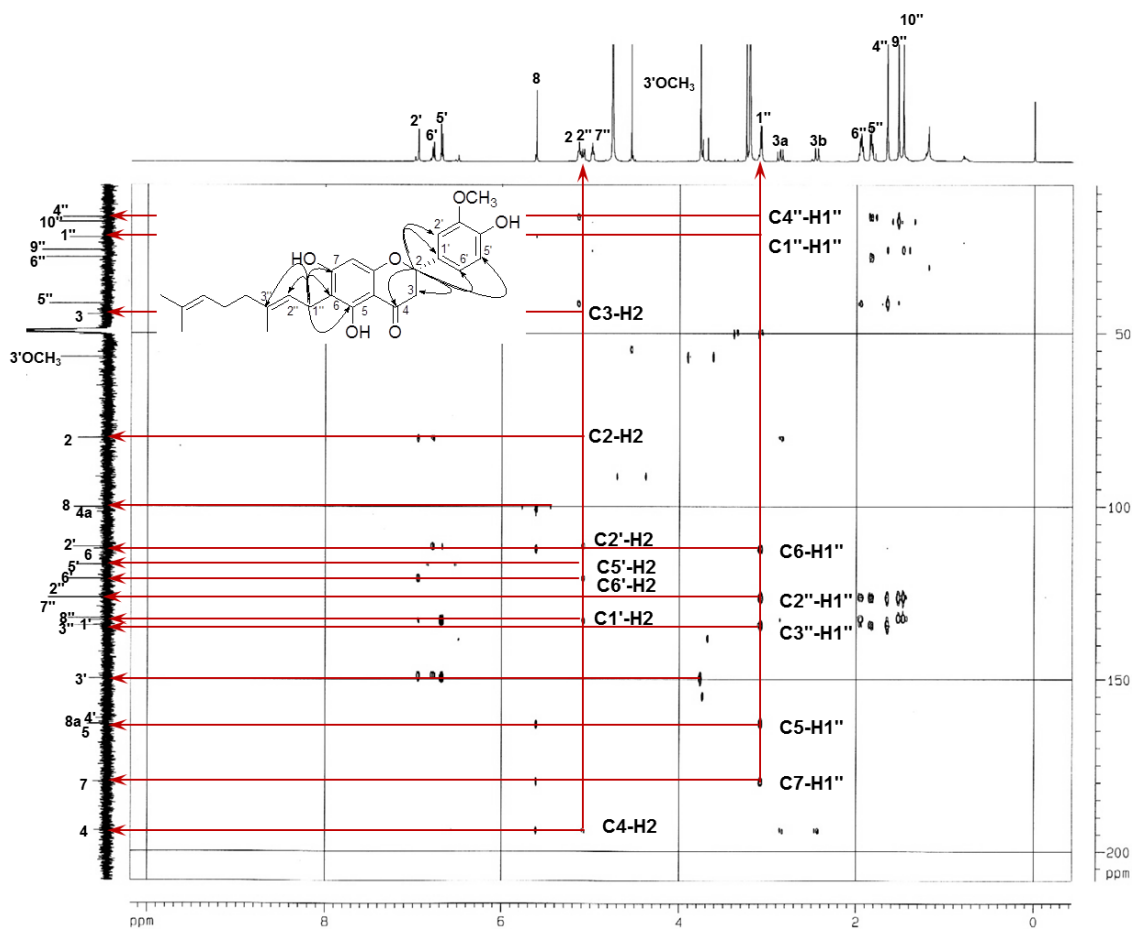


Figure 15. HMBC spectrum of compound 2.

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[ Elemental Composition ]
Data :
Sample: -
Note : -
Inlet : Direct
RT : 2.50 min
Elements : C 100/1, H 100/1, O 20/1
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 10mmu if m/z > 10
Unsaturation (U.S.) : 5.0 - 30.0
Ion Mode : EI+
Scan#: 76
```

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
438.2035	100.0	+11.6 / +5.1	21.0	C 33 H 26 O
		-1.8 / -0.8	12.0	C 26 H 30 O 6

Figure 16. HREIMS data of compound 2.

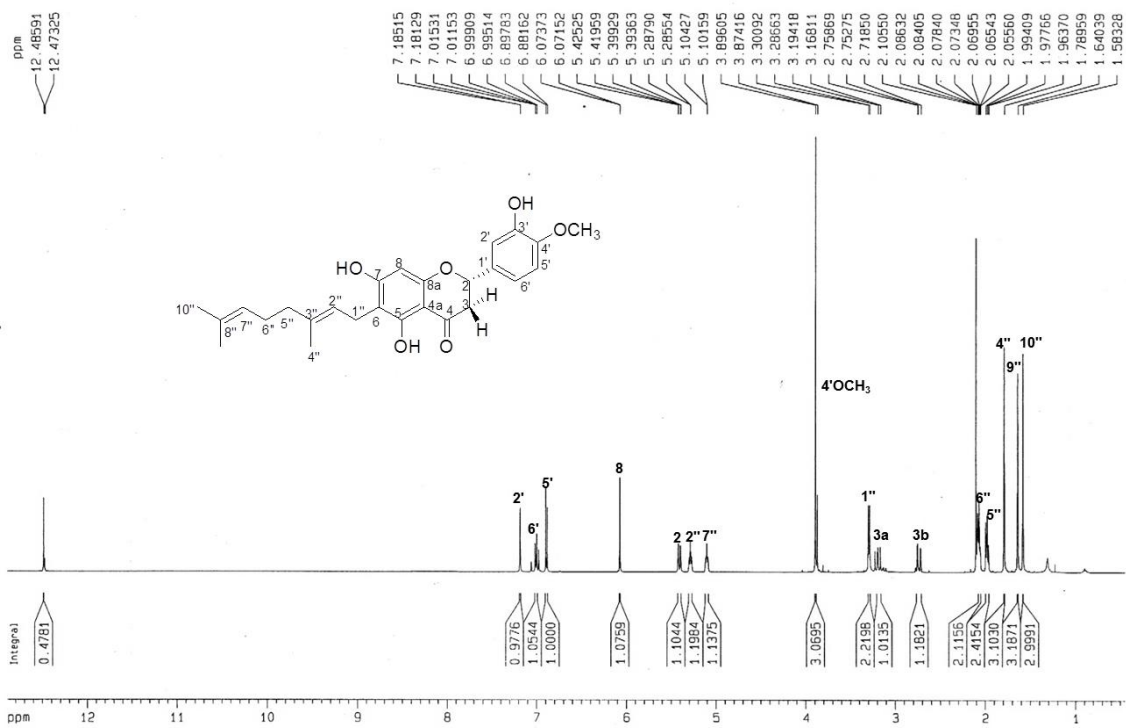


Figure 17.  $^1\text{H-NMR}$  spectrum of compound 3 (500MHz, Aceton- $d_6$ ).

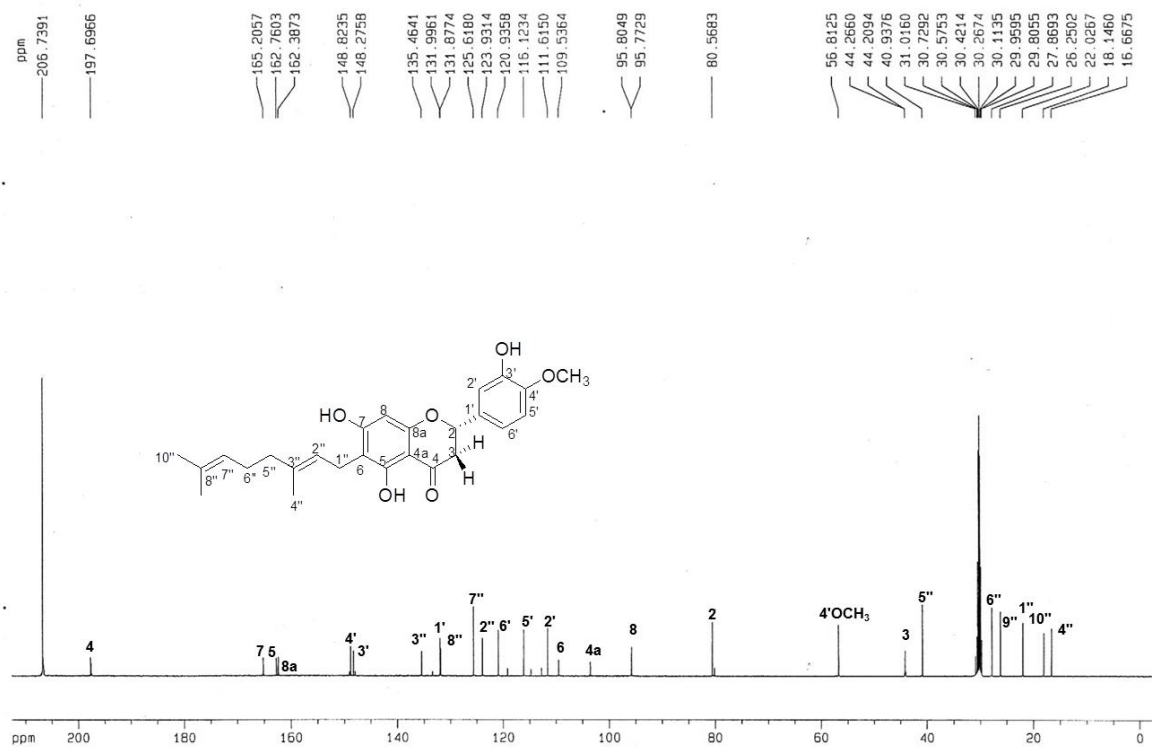


Figure 18.  $^{13}\text{C-NMR}$  spectrum of compound 3 (125MHz, Aceton- $d_6$ ).

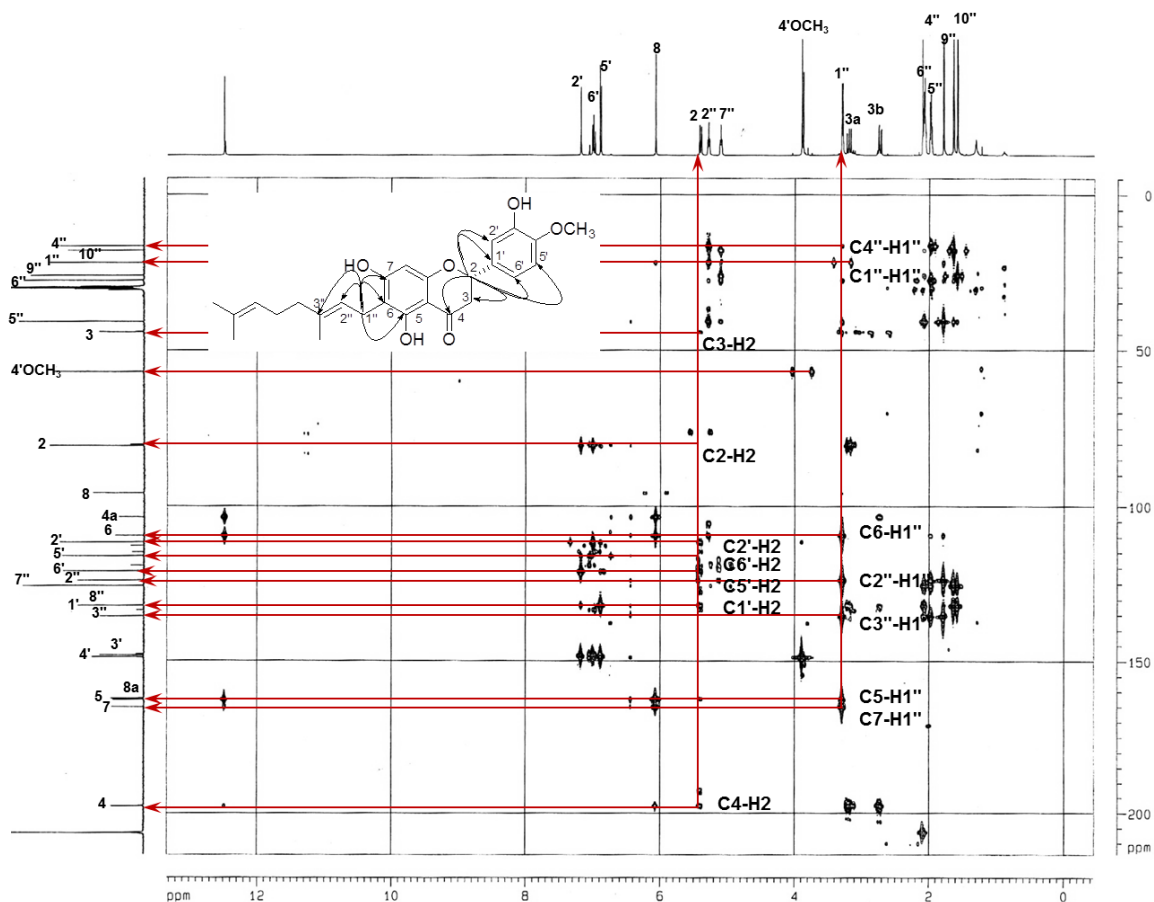


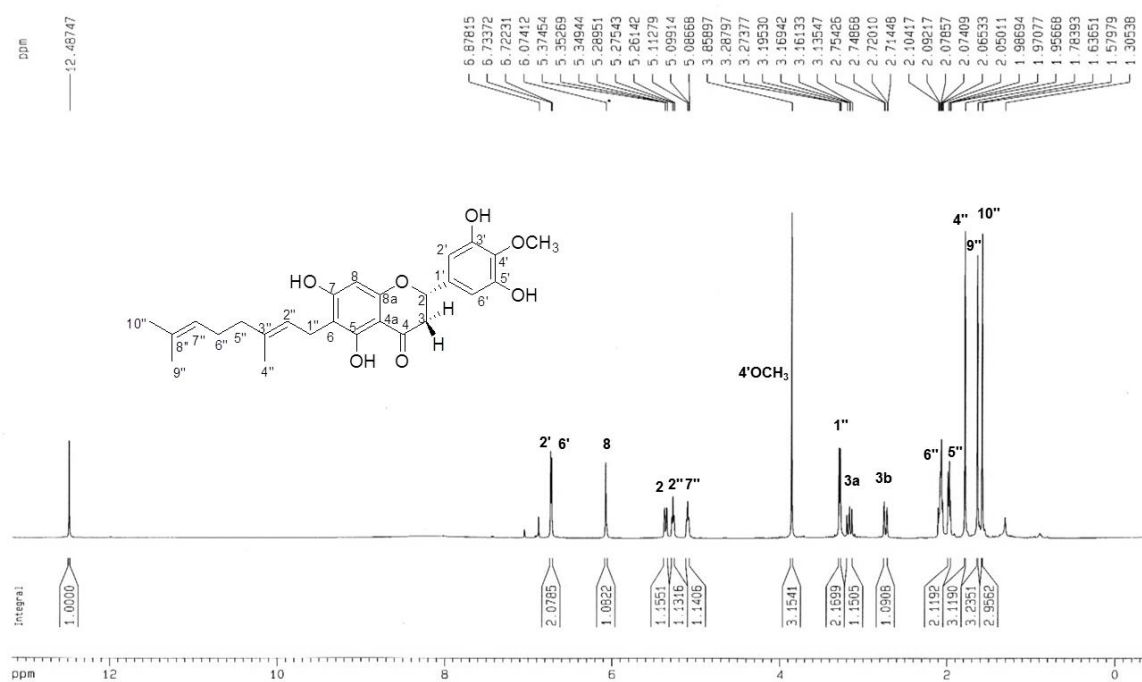
Figure 19. HMBC spectrum of compound 3.

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[ Elemental Composition ]
Data :
Sample: - *
Note : -
Inlet : Direct
RT : 1.90 min
Elements : C 100/1, H 100/1, O 20/1
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 10mmu if m/z > 10
Unsaturation (U.S.) : 5.0 - 30.0

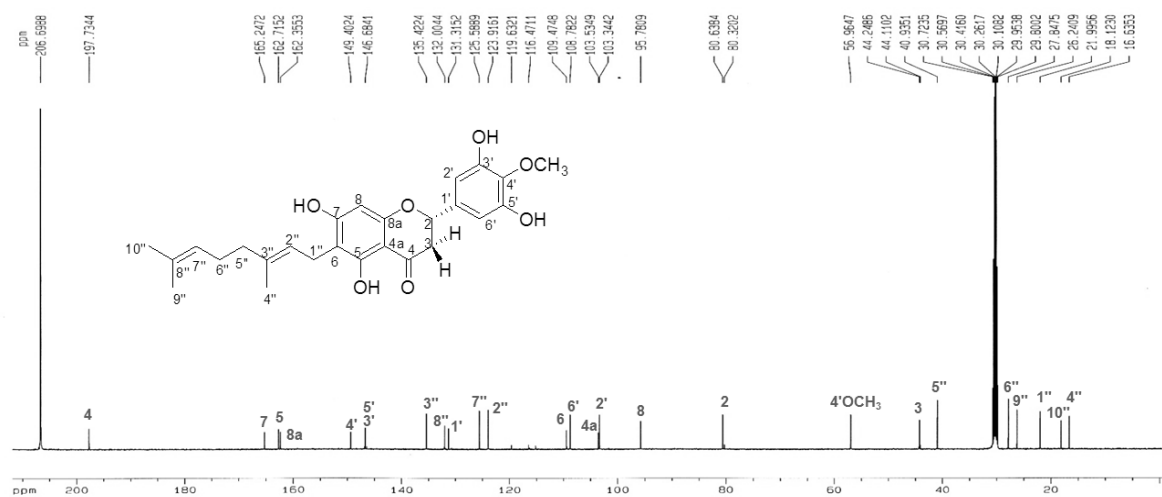
Ion Mode : EI+
Scan#: 58

Observed m/z Int% Err[ppm / mmu] U.S. Composition
438.2040 100.0 +13.0 / +5.7 21.0 C 33 H 26 O
-0.5 / -0.2 12.0 C 26 H 30 O 6
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Figure 20. HREIMS data of compound 3.



**Figure 21.**  $^1\text{H-NMR}$  spectrum of compound **4** (500MHz, Aceton- $d_6$ ).



**Figure 22.**  $^{13}\text{C-NMR}$  spectrum of compound **4** (125MHz, Aceton- $d_6$ ).

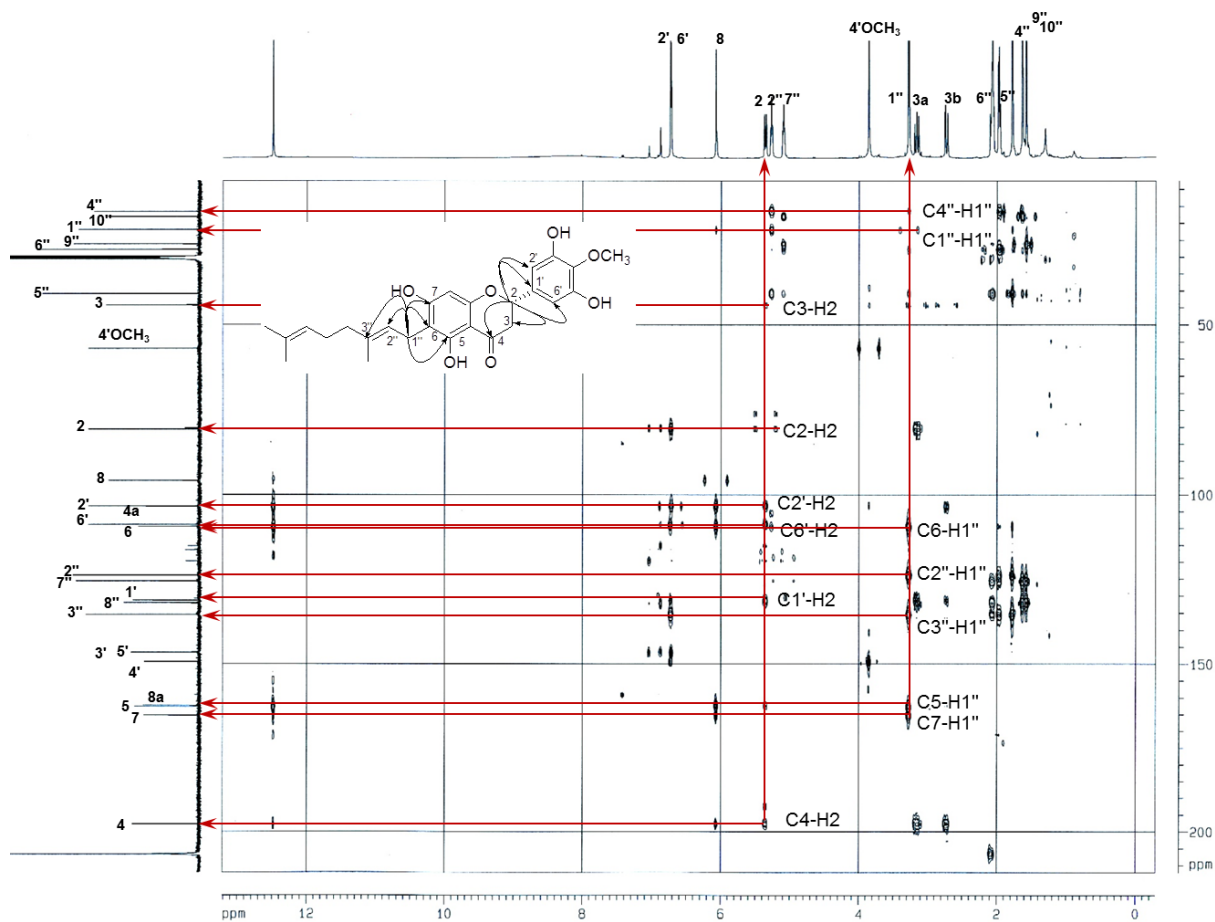


Figure 23. HMBC spectrum of compound 4.

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[ Elemental Composition ]
Data :
Sample: -
Note : -
Inlet : Direct           Ion Mode : EI+
RT : 1.95 min           Scan#: 40
Elements : C 100/1, H 100/0, O 20/1
Mass Tolerance : 1000ppm, 3mmu if m/z < 3, 5mmu if m/z > 5
Unsaturation (U.S.) : 3.0 - 30.0
```

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
424.1947	71.8	+0.6 / +0.2	3.0	C 18 H 32 O 11
425.1989	27.4	+5.7 / +2.4	11.5	C 25 H 29 O 6
429.0897	15.3	-4.3 / -1.8	26.5	C 32 H 13 O 2
		+3.9 / +1.7	4.5	C 14 H 21 O 15
454.1992	100.0	+0.1 / +0.0	12.0	C 26 H 30 O 7

Figure 24. HREIMS data of compound 4.

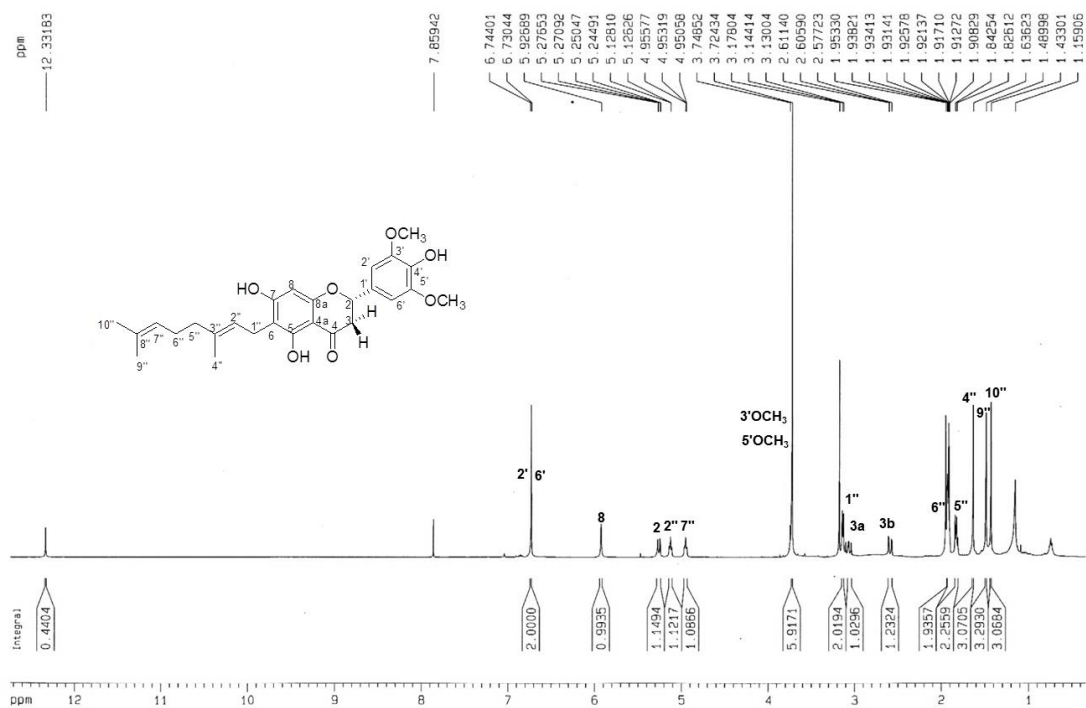


Figure 25.  $^1\text{H-NMR}$  spectrum of compound **5** (500MHz, Aceton- $d_6$ ).

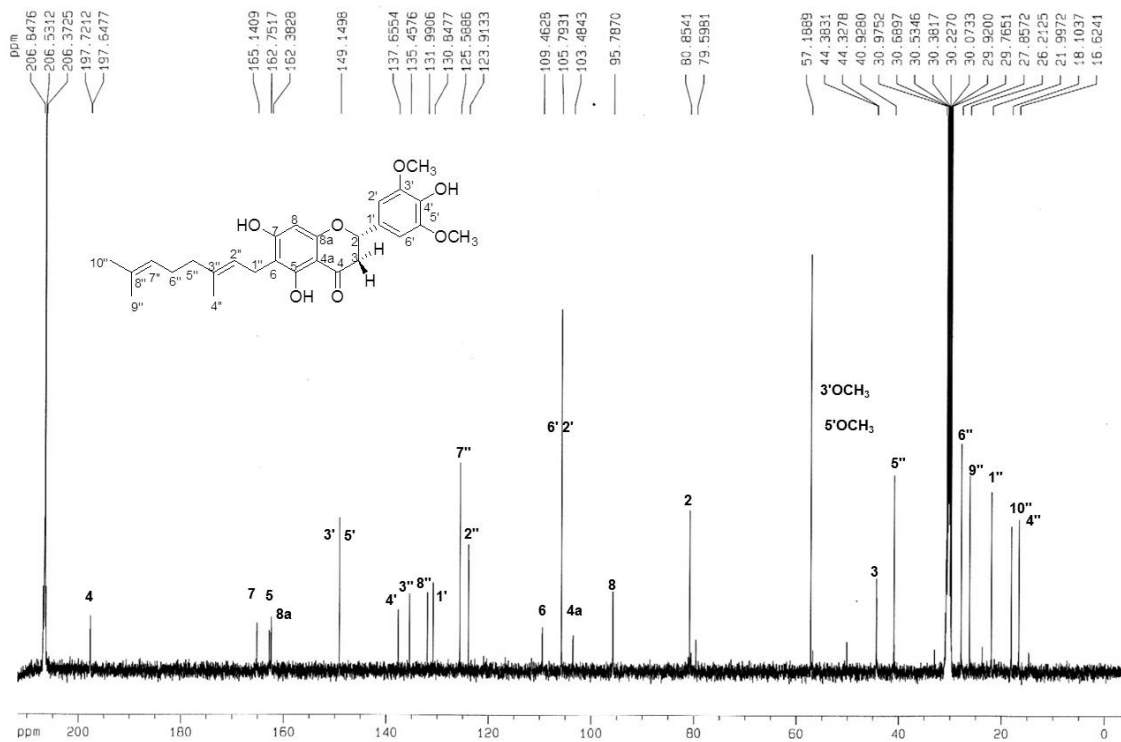


Figure 26.  $^{13}\text{C-NMR}$  spectrum of compound **5** (125MHz, Aceton- $d_6$ ).

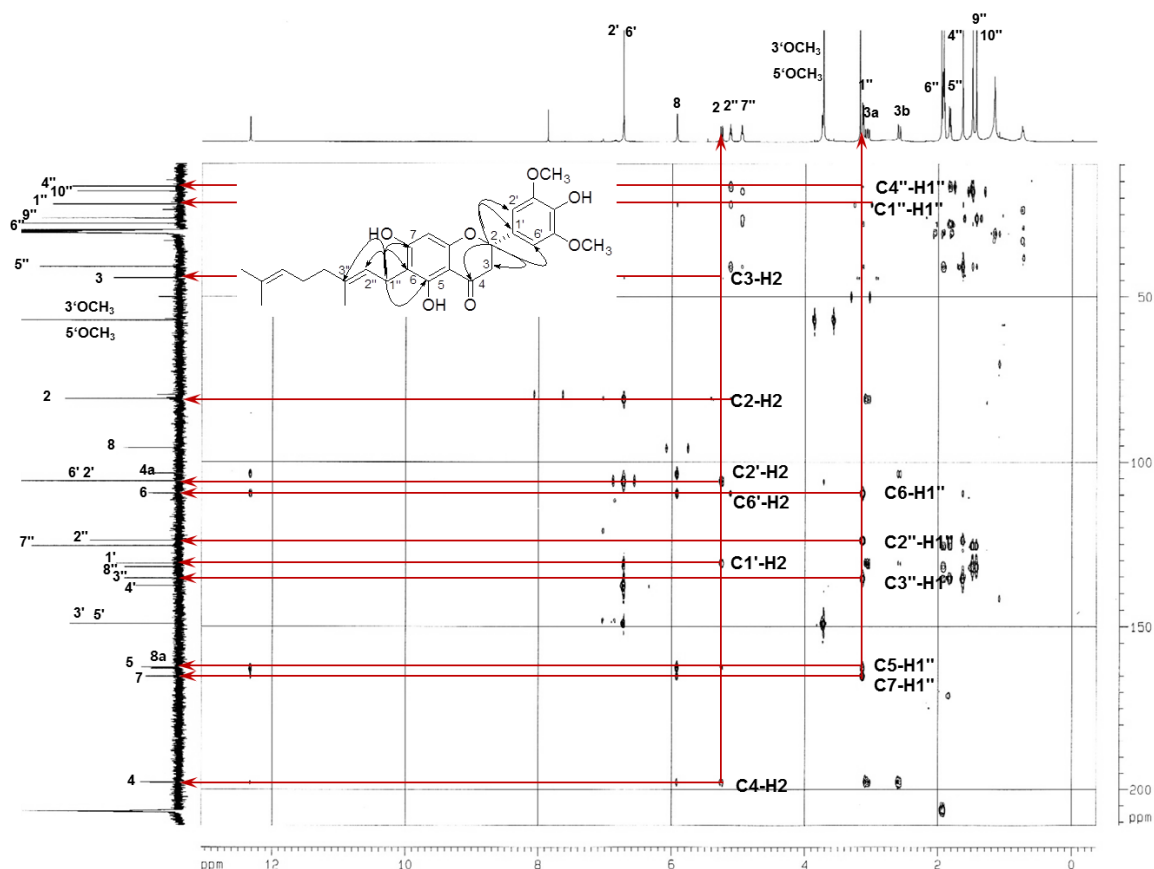


Figure 27. HMBC spectrum of compound 5.

```
[ Elemental Composition ]
Data :
Sample: -
Note : -
Inlet : Direct
RT : 1.30 min
Elements : C 100/1, H 100/1, O 20/1
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 10mmu if m/z > 10
Unsaturation (U.S.) : 5.0 - 30.0
Ion Mode : EI+
Scan#: 40
```

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
468.2151	100.0	+13.3 / +6.2	21.0	C 34 H 28 O 2
		+0.7 / +0.3	12.0	C 27 H 32 O 7

Figure 28. HREIMS data of compound 5.



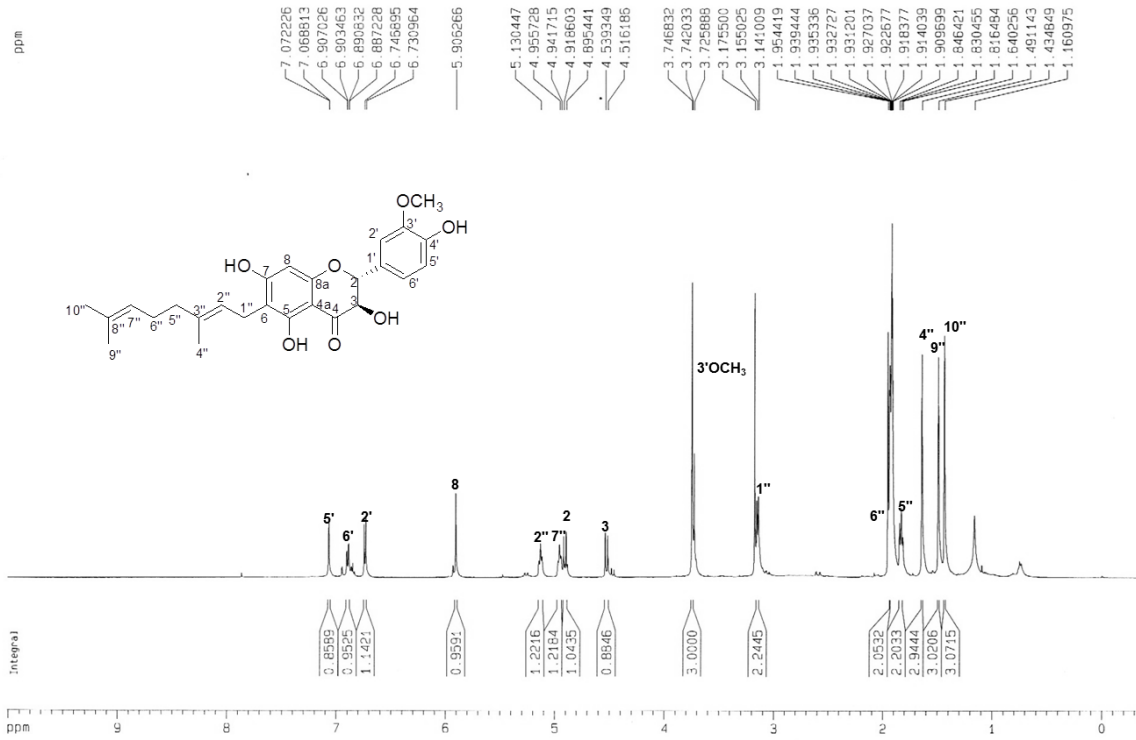


Figure 29. <sup>1</sup>H-NMR spectrum of compound 6 (500MHz, Aceton-d<sub>6</sub>).

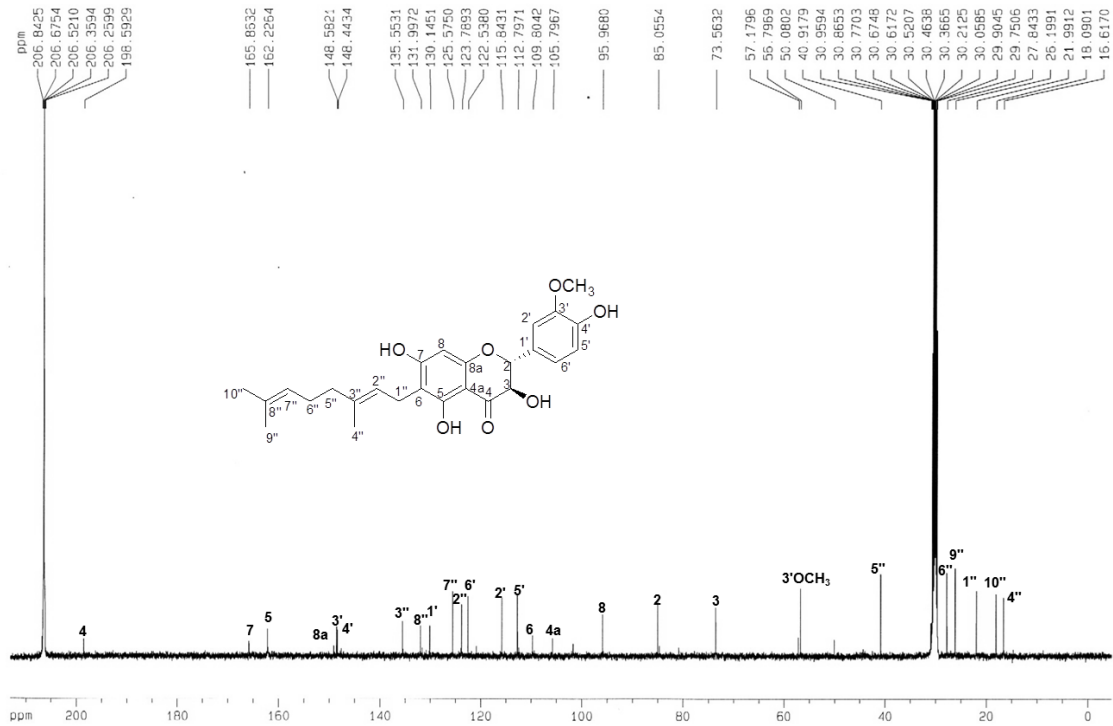


Figure 30. <sup>13</sup>C-NMR spectrum of compound 6 (125MHz, Aceton-d<sub>6</sub>).

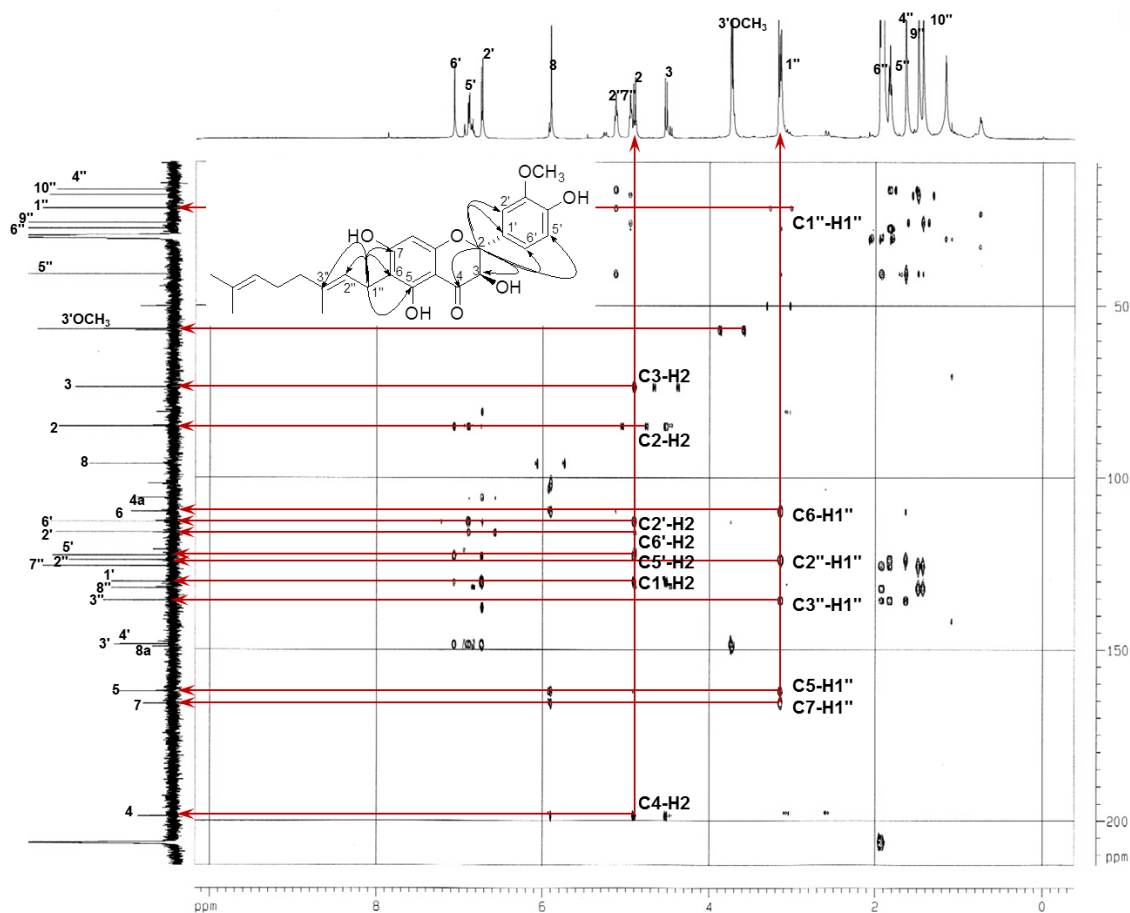


Figure 31. HMBC spectrum of compound 6.

[ Elemental Composition ]  
 Data :  
 Sample: -  
 Note : -  
 Inlet : Direct  
 RT : 2.00 min  
 Elements : C 100/1, H 100/0, O 20/1  
 Mass Tolerance : 1000ppm, 3mmu if m/z < 3, 10mmu if m/z > 10  
 Unsaturation (U.S.) : 3.0 - 30.0

Ion Mode : EI+  
 Scan#: 41

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
454.1990	100.0	+12.6 / +5.7	21.0	C 33 H 26 O 2
		-0.3 / -0.1	12.0	C 26 H 30 O 7
		-13.3 / -6.0	3.0	C 19 H 34 O 12

Figure 32. HREIMS data of compound 6.

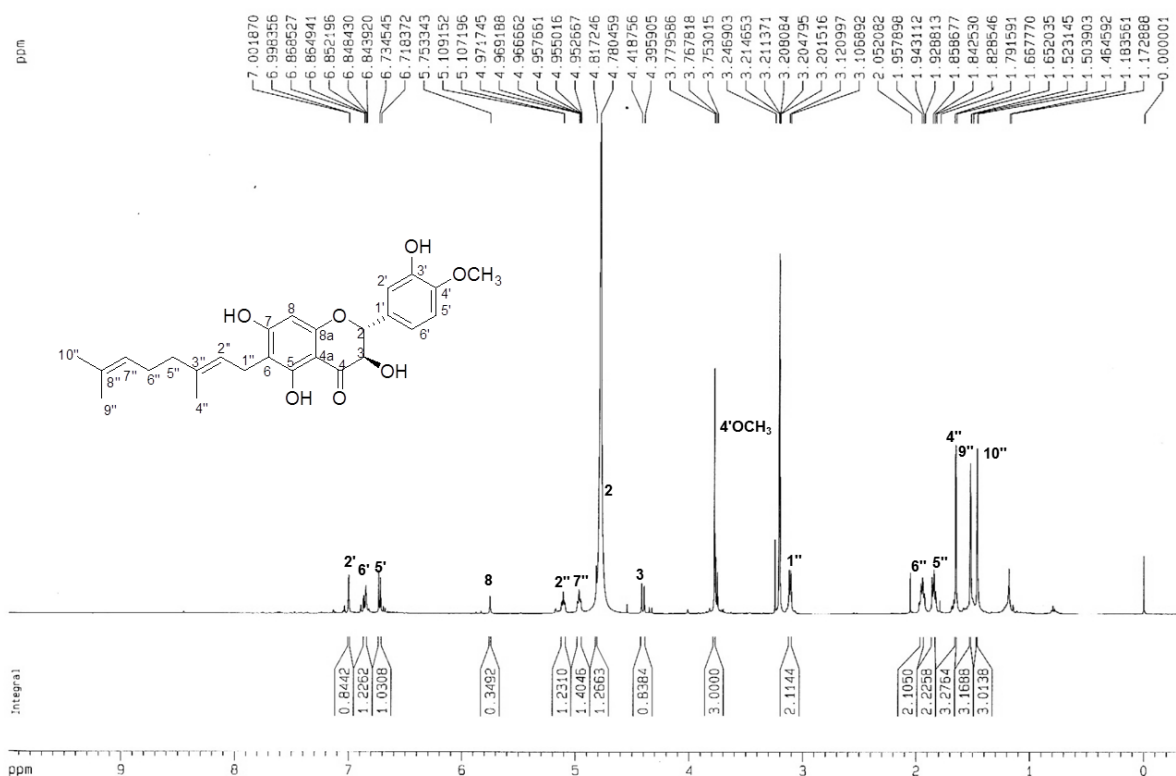


Figure 33.  $^1\text{H-NMR}$  spectrum of compound 7 (500MHz,  $\text{CD}_3\text{OD}$ ).

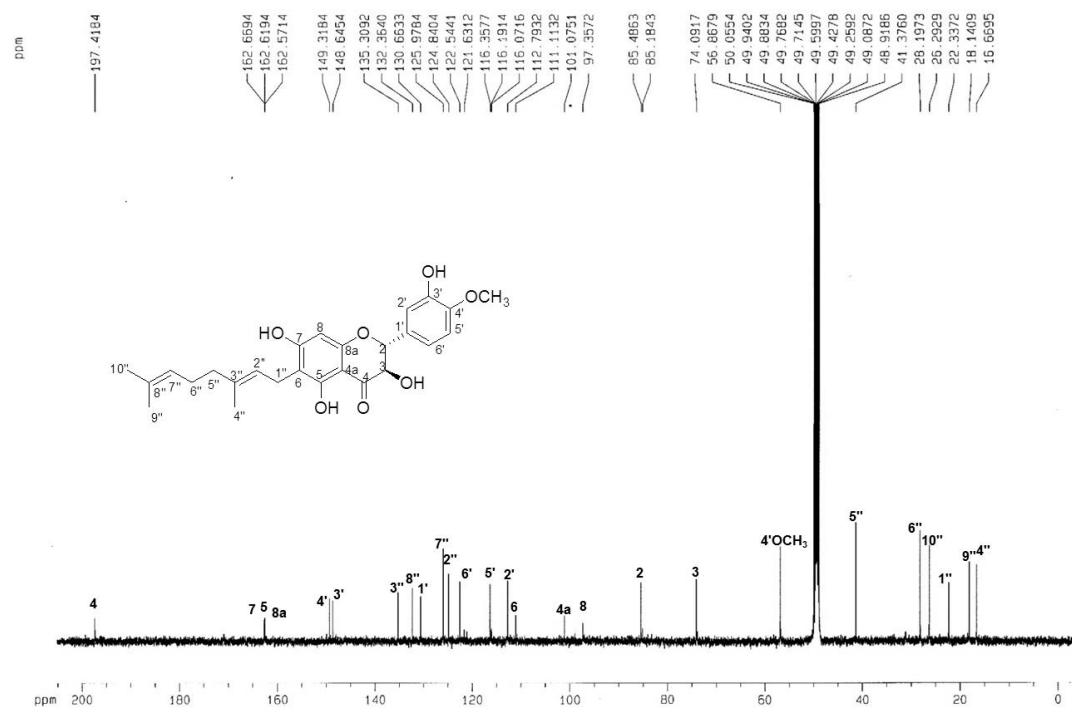


Figure 34.  $^{13}\text{C-NMR}$  spectrum of compound 7 (125MHz,  $\text{CD}_3\text{OD}$ ).

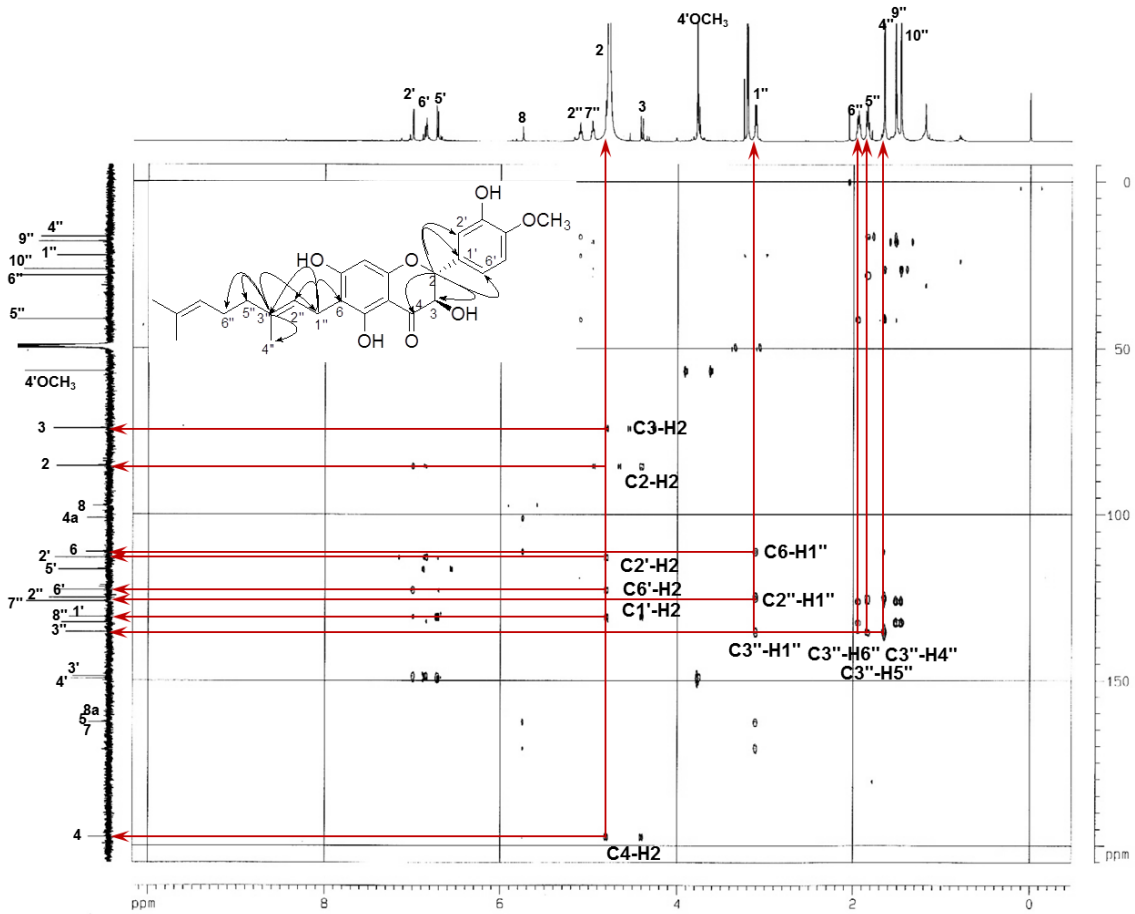


Figure 35. HMBC spectrum of compound 7.

[ Elemental Composition ]

Data :

Sample: -

Note: -

Inlet: Direct

Ion Mode: EI+

RT: 1.24 min

Scan#: 38

Elements: C 100/1, H 100/1, O 20/1

Mass Tolerance: 1000ppm, 1mmu if m/z < 1, 10mmu if m/z > 10

Unsaturation (U.S.): 5.0 - 30.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
454.1993	100.0	+13.3 / +6.0	21.0	C 33 H 26 O 2
		+0.3 / +0.2	12.0	C 26 H 30 O 7

Figure 36. HREIMS data of compound 7.

Compound **1** (*Mimulone*); colorless powder; mp > 116°C; EIMS,  $m/z$  408 [M]<sup>+</sup>; HREIMS,  $m/z$  408.1938 (calcd for C<sub>25</sub>H<sub>28</sub>O<sub>5</sub> 408.1937); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 1.52 (3H, s, H-10), 1.60 (3H, s, H-9''), 1.73 (3H, s, H-4''), 1.99 (2H, m, H-5''), 2.02 (2H, m, H-6''), 2.70 (1H, dd,  $J$  = 2.6, 17.1 Hz, H-3b), 3.00 (1H, dd,  $J$  = 13.0, 17.1 Hz, H-3a), 3.26 (2H, d,  $J$  = 7.0 Hz, H-1''), 5.18 (1H, t, H-2''), 5.24 (1H, dd,  $J$  = 2.5, 13.0 Hz, H-2), 5.92 (1H, s, H-8), 6.79 (1H, s, H-5'), 6.80 (1H, s, H-3'), 7.22 (1H, s, H-6'), 7.24 (1H, s, H-2'). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) δ 16.6 (C-4''), 18.1 (C-10''), 21.5 (C-1''), 26.1 (C-9''), 26.8 (C-6''), 40.1 (C-5''), 43.6 (C-3), 79.2 (C-2), 96.1 (C-8), 103.3 (C-4a), 107.4 (C-6), 116.1 (C-3'), 116.1 (C-5'), 121.7 (C-2'), 124.1 (C-7'), 128.3 (C-2'), 128.3 (C-6'), 131.0 (C-1'), 132.5 (C-8''), 139.7 (C-3''), 156.6 (C-4'), 161.5 (C-8a), 161.7 (C-5), 164.5 (C-7), 196.7 (C=O, C-4).

Compound **2** (*3'-O-methyldiplacone*); colorless powder; mp > 103°C; EIMS,  $m/z$  438 [M]<sup>+</sup>; HREIMS,  $m/z$  438.2035 (calcd for C<sub>26</sub>H<sub>30</sub>O<sub>6</sub> 438.2042); <sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>OD) δ 1.47 (3H, s, H-10''), 1.53 (3H, s, H-9''), 1.65 (3H, s, H-4''), 1.84 (2H, m, H-5''), 1.95 (2H, m, H-6''), 2.45 (1H, dd,  $J$  = 3.1, 17.0 Hz, H-3b), 2.85 (1H, dd,  $J$  = 12.5, 17.0 Hz, H-3a), 3.08 (2H, d,  $J$  = 6.9 Hz, H-1''), 3.77 (3H, s, H-3'OCH<sub>3</sub>), 4.99 (1H, t, H-7''), 5.08 (1H, dd,  $J$  = 3.1, 12.5 Hz, H-2), 5.14 (1H, t, H-2''), 5.62 (1H, s, H-8), 6.69 (1H, d,  $J$  = 8.0 Hz, H-5'), 6.78 (1H, dd,  $J$  = 1.8, 8.0 Hz, H-6'), 6.94 (1H, d,  $J$  = 1.8 Hz, H-2'). <sup>13</sup>C-NMR (125 MHz, CD<sub>3</sub>OD) δ 16.7 (C-4''), 18.1 (C-10''), 22.6 (C-1''), 26.3 (C-9''), 28.3 (C-6''), 41.5 (C-5''), 44.5 (C-3), 56.8 (OCH<sub>3</sub>-3'), 80.4 (C-2), 100.2 (C-8), 100.7 (C-4a), 111.5 (C-2'), 112.2 (C-6), 116.7 (C-5'), 120.7 (C-6'), 126.2 (C-2''), 126.2 (C-7''), 132.2 (C-8''), 132.8 (C-1'), 134.2 (C-3''), 149.7 (C-3'), 161.3 (C-4'), 162.9 (C-8a), 163.1 (C-5), 179.8 (C-7), 194.0 (C=O, C-4).

Compound **3** (*4'-O-methyldiplacone*); pale yellow powder; mp > 102°C; EIMS, *m/z* 438 [M]<sup>+</sup>; HREIMS, *m/z* 438.2040 (calcd for C<sub>26</sub>H<sub>30</sub>O<sub>6</sub> 438.2042); <sup>1</sup>H-NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 1.58 (3H, s, H-10''), 1.64 (3H, s, H-9''), 1.79 (3H, s, H-4''), 1.98 (2H, m, H-5''), 2.07 (2H, m, H-6''), 2.74 (1H, dd, *J* = 3.0, 17.1 Hz, H-3b), 3.18 (1H, dd, *J* = 13.0, 17.1 Hz, H-3a), 3.30 (2H, d, *J* = 7.2 Hz, H-1''), 3.90 (3H, s, H-4'OCH<sub>3</sub>), 5.10 (1H, t, H-7''), 5.29 (1H, t, H-2''), 5.41 (1H, dd, *J* = 2.8, 13.0 MHz, H-2), 6.07 (1H, s, H-8), 6.89 (1H, d, *J* = 8.1 Hz, H-5'), 7.00 (1H, dd, *J* = 1.9, 8.1 Hz, H-6'), 7.18 (1H, d, *J* = 1.9 Hz, H-2'). <sup>13</sup>C-NMR (125 MHz, acetone-*d*<sub>6</sub>) δ 16.7 (C-4''), 18.2 (C-10''), 22.0 (C-1''), 26.3 (C-9''), 27.9 (C-6''), 40.9 (C-5''), 44.3 (C-3), 56.8 (OCH<sub>3</sub>-4'), 80.6 (C-2), 95.8 (C-8), 103.6 (C-4a), 109.5 (C-6), 111.6 (C-2'), 116.1 (C-5'), 120.9 (C-6'), 123.9 (C-2''), 125.6 (C-7''), 131.9 (C-8''), 132.0 (C-1'), 135.5 (C-3''), 148.3 (C-3'), 148.8 (C-4'), 162.4 (C-8a), 162.8 (C-5), 165.2 (C-7), 197.7 (C=O, C-4).

Compound **4** (*6-Geranyl-3',5,5',7-tetrahydroxy-4'-methoxyflavanone*); colorless powder; mp > 108°C; EIMS, *m/z* 454 [M]<sup>+</sup>; HREIMS, *m/z* 454.1992 (calcd for C<sub>26</sub>H<sub>30</sub>O<sub>7</sub> 454.1992); <sup>1</sup>H-NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 1.58 (3H, s, H-10''), 1.64 (3H, s, H-9''), 1.78 (3H, s, H-4''), 1.97 (2H, t, *J* = 7.0, 8.1 Hz, H-5''), 2.06 (2H, t, *J* = 4.4, 12.0 Hz, H-6''), 2.73 (1H, dd, *J* = 2.8, 17.1 Hz, H-3b), 3.16 (1H, dd, *J* = 13.0, 10.9 Hz, H-3a), 3.28 (2H, d, *J* = 7.1 Hz, H-1''), 3.86 (3H, s, H-4'OCH<sub>3</sub>), 5.09 (1H, t, *J* = 6.2, 6.8 Hz, H-7''), 5.26 (1H, d, *J* = 10.9 Hz, H-2), 5.27 (1H, t, *J* = 7.0, 14.1 Hz, H-2''), 6.07 (1H, s, H-8), 6.72 (1H, s, H-6'), 6.73 (1H, s, H-2'); <sup>13</sup>C-NMR (125 MHz, acetone-*d*<sub>6</sub>) δ 16.6 (C-4''), 18.1 (C-10''), 22.0 (C-1''), 26.2 (C-9''), 27.9 (C-5''), 40.9 (C-6''), 44.3 (C-3), 57.0 (C-4'OCH<sub>3</sub>), 80.6 (C-2), 95.8 (C-8), 103.3 (C-2'), 103.5 (C-4a), 108.8 (C-6'), 109.5 (C-6), 123.9 (C-2''), 125.6 (C-7''), 131.3 (C-1'), 132.0 (C-8''), 135.4 (C-3''), 146.7 (C-3', 5'), 149.4 (C-4'), 162.4 (C-8a), 162.7 (C-5), 165.3 (C-7), 197.7 (C-4).

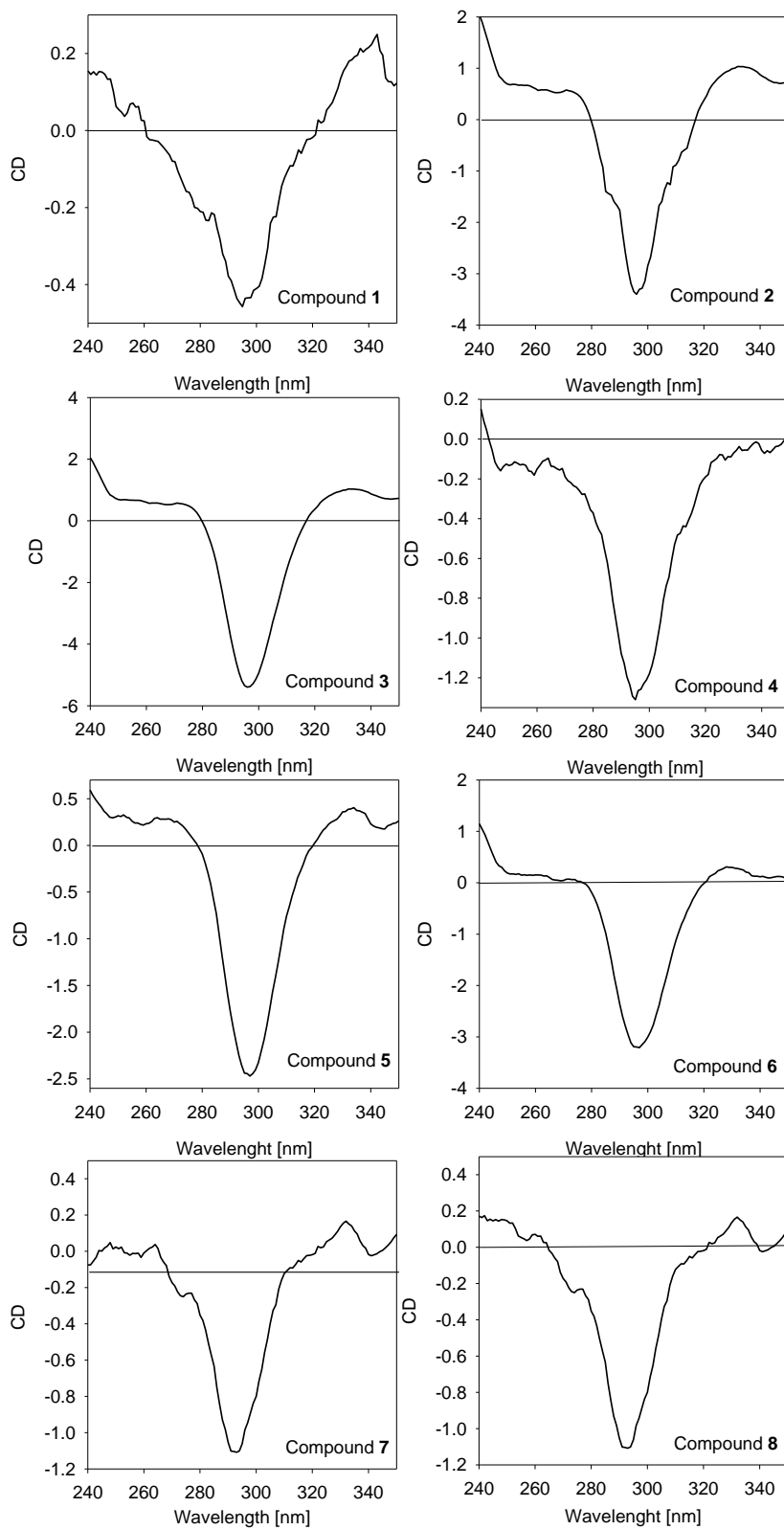
Compound **5** (*3'-O-Methyl-5'-O-methyldiplacone*); colorless powder; mp > 78°C; EIMS,  $m/z$  468 [M]<sup>+</sup>; HREIMS,  $m/z$  468.2151 (calcd for C<sub>27</sub>H<sub>32</sub>O<sub>7</sub> 468.2148). <sup>1</sup>H-NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 1.43 (3H, s, H-10''), 1.49 (3H, s, H-9''), 1.64 (3H, s, H-4''), 1.83 (2H, m, H-5''), 1.93 (2H, m, H-6''), 2.59 (1H, dd,  $J = 2.8, 17.1$  Hz, H-3b), 3.06 (1H, dd,  $J = 13.0, 17.1$  Hz, H-3a), 3.14 (2H, d,  $J = 7.1$  Hz, H-1''), 3.72 (3H, s, H-3'OCH<sub>3</sub>), 3.72 (3H, s, H-5'OCH<sub>3</sub>), 4.95 (1H, t, H-7''), 5.13 (1H, t, H-2''), 5.26 (1H, dd,  $J = 2.8, 13.0$ , H-2), 5.93 (1H, s, H-8), 6.73 (1H, s, H-2'), 6.73 (1H, s, H-6'). <sup>13</sup>C-NMR (125 MHz, acetone-*d*<sub>6</sub>) δ 16.6 (C-4''), 18.1 (C-10''), 22.0 (C-1''), 26.2 (C-9''), 27.9 (C-6''), 40.9 (C-5''), 44.4 (C-3), 57.2 (OCH<sub>3</sub>-3'), 57.2 (OCH<sub>3</sub>-5'), 80.9 (C-2), 95.8 (C-8), 103.5 (C-4a), 105.8 (C-2'), 105.8 (C-6'), 109.5 (C-6), 123.8 (C-2''), 125.6 (C-7''), 130.2 (C-1'), 132.0 (C-8''), 135.5 (C-3''), 137.7 (C-4'), 149.2 (C-3'), 149.2 (C-5'), 162.4 (C-8a), 162.8 (C-5), 165.1 (C-7), 197.7 (C=O, C-4).

Compound **6** (*3'-O-methyldiplacol*); pale yellow powder; mp > 140°C; EIMS,  $m/z$  454 [M]<sup>+</sup>; HREIMS,  $m/z$  454.1990 (calcd for C<sub>26</sub>H<sub>30</sub>O<sub>7</sub> 454.1992); <sup>1</sup>H-NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 1.43 (3H, s, H-10''), 1.49 (3H, s, H-9''), 1.64 (3H, s, H-4''), 1.82 (2H, m, H-5''), 1.94 (2H, m, H-6''), 3.15 (2H, d,  $J = 7.1$  Hz, H-1''), 3.74 (3H, s, H-3'OCH<sub>3</sub>), 4.53 (1H, d,  $J = 11.6$  Hz, H-3), 4.91 (1H, d,  $J = 11.6$  Hz, H-2), 4.95 (1H, t, H-7''), 5.12 (1H, t, H-2''), 5.91 (1H, s, H-8), 6.74 (1H, d,  $J = 8.0$  Hz, H-2'), 6.89 (1H, dd,  $J = 1.7, 8.0$  Hz, H-6'), 7.07 (1H, d,  $J = 1.7$  Hz, H-5'). <sup>13</sup>C-NMR (125 MHz, acetone-*d*<sub>6</sub>) δ 16.6 (C-4''), 18.1 (C-10''), 22.0 (C-1''), 26.2 (C-9''), 27.8 (C-6''), 40.9 (C-5''), 56.8 (OCH<sub>3</sub>-3'), 80.8 (C-3), 85.1 (C-2), 96.0 (C-8), 105.8 (C-4a), 109.8 (C-6), 112.8 (C-5'), 115.8 (C-2'), 122.5 (C-6'), 123.8 (C-2''), 125.6 (C-7''), 130.2 (C-1'), 132.0 (C-8''), 135.6 (C-3''), 148.4 (C-4'), 148.6 (C-3'), 149.8 (C-8a), 162.2 (C-5), 165.9 (C-7), 198.6 (C=O, C-4).

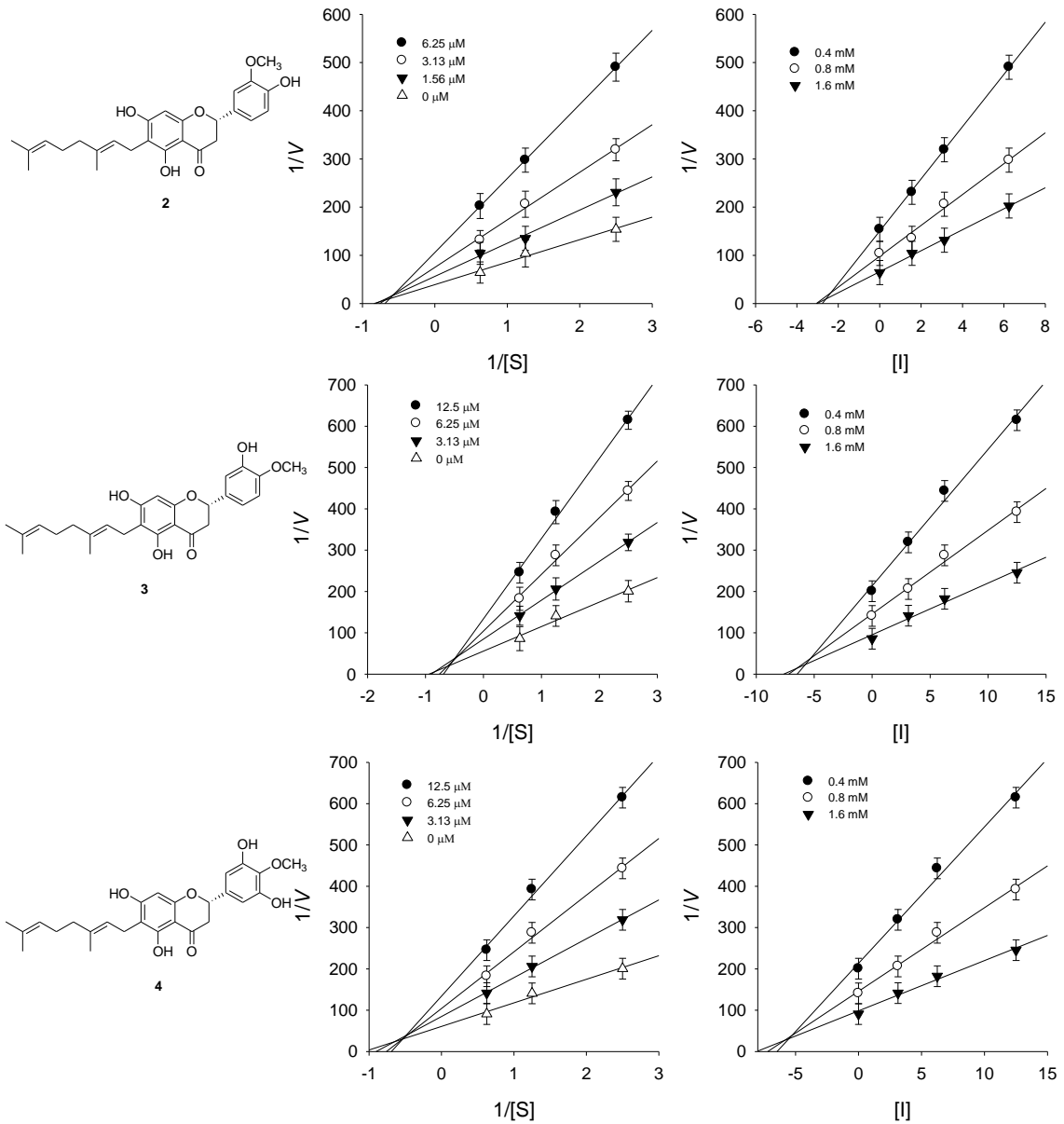


Compound **7** (*4'-O-methyldiplacol*); pale yellow powder; mp > 140°C; EIMS, *m/z* 454 [M]<sup>+</sup>; HREIMS, *m/z* 454.1993 (calcd for C<sub>26</sub>H<sub>30</sub>O<sub>7</sub> 454.1992); <sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>OD) δ 1.46 (3H, s, H-10''), 1.52 (3H, s, H-9''), 1.67 (3H, s, H-4''), 1.84 (2H, m, H-5''), 1.94 (2H, m, H-6''), 3.11 (2H, d, *J* = 7.1 Hz, H-1''), 3.78 (3H, s, H-4'OCH<sub>3</sub>), 4.41 (1H, d, *J* = 10.8 Hz, H-3), 4.82 (1H, d, *J* = 10.8 Hz, H-2), 5.10 (1H, t, H-7''), 5.12 (1H, t, H-2''), 5.75 (1H, s, H-8), 6.73 (1H, d, *J* = 8.1 Hz, H-5'), 6.85 (1H, dd, *J* = 1.8, 8.1 Hz, H-6'), 7.00 (1H, d, *J* = 1.8 Hz, H-2'). <sup>13</sup>C-NMR (125 MHz, CD<sub>3</sub>OD) δ 16.7 (C-4''), 18.1 (C-9''), 22.3 (C-1''), 26.3 (C-10''), 28.2 (C-6''), 41.4 (C-5''), 56.9 (OCH<sub>3</sub>-4'), 74.1 (C-3), 85.5 (C-2), 97.4 (C-8), 101.1 (C-4a), 111.1 (C-6), 112.8 (C-2'), 116.4 (C-5'), 122.5 (C-6'), 124.8 (C-2''), 126.0 (C-7''), 130.7 (C-1'), 132.4 (C-8''), 135.3 (C-3''), 148.6 (C-3'), 149.3 (C-4'), 162.5 (C-8a), 162.6 (C-5), 162.7 (C-7), 197.4 (C=O, C-4).

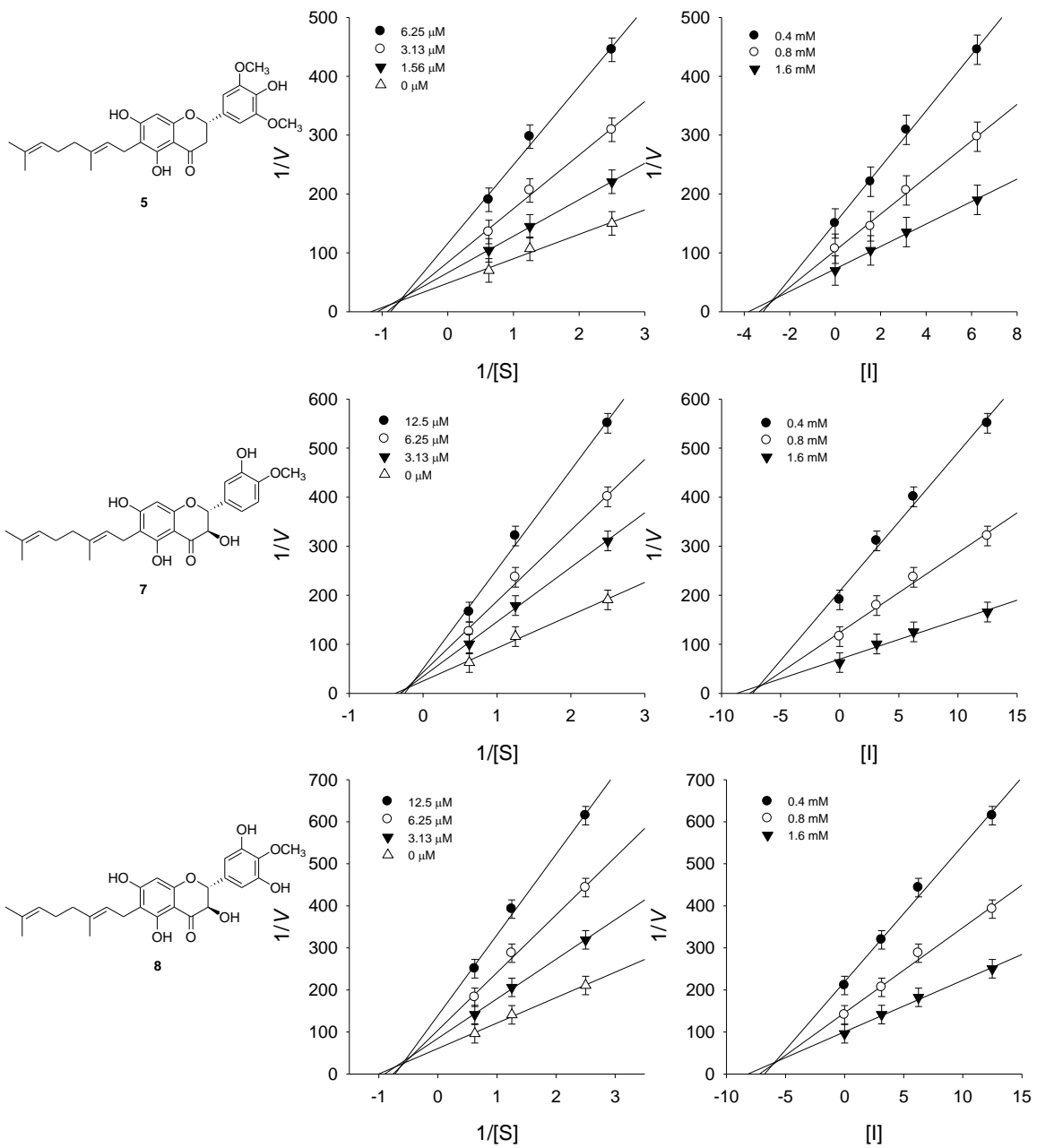
Compound **8** (*6-Geranyl-3,3',5,5',7-pentahydroxy-4'-methoxyflavane*); white needles; EIMS, *m/z* 470 [M]<sup>+</sup>; HREIMS, *m/z* 470.1943 (calcd for C<sub>26</sub>H<sub>30</sub>O<sub>8</sub> 470.1941); <sup>1</sup>H-NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 1.44 (3H, s, H-10''), 1.49 (3H, s, H-9''), 1.64 (3H, s, H-4''), 1.83 (2H, t, *J* = 7.0, 8.2 Hz, H-6''), 1.92 (2H, d, *J* = 2.2 Hz, H-5''), 3.15 (2H, d, *J* = 7.1 Hz, H-1''), 3.71 (2H, s, H-4'OCH<sub>3</sub>), 4.49 (1H, d, *J* = 11.4 Hz, H-3), 4.84 (1H, d, *J* = 11.4 Hz, H-2), 4.96 (1H, dd, *J* = 5.6, 7.0 Hz, H-7''), 5.13 (1H, t, *J* = 1.1, 6.1 Hz, H-2''), 5.91 (2H, s, H-8), 6.62 (2H, d, *J* = 4.2 Hz, H-2', 6'); <sup>13</sup>C-NMR (125 MHz, acetone-*d*<sub>6</sub>) δ 16.6 (C-4''), 18.1 (C-10''), 22.0 (C-1''), 26.2 (C-9''), 27.8 (C-6''), 40.9 (C-5''), 57.0 (C-4'OCH<sub>3</sub>), 73.7 (C-3), 85.3 (C-2), 96.0 (C-8), 101.8 (C-4a), 104.9 (C-6'), 109.8 (C-6), 110.2 (C-2'), 123.8 (C-2''), 125.6 (C-7''), 129.5 (C-1'), 132.0 (C-8''), 135.5 (C-3'), 135.7 (C-3''), 146.5 (C-5'), 149.2 (C-4'), 162.2 (C-8a), 162.4 (C-5), 165.9 (C-7), 198.64 (C-4).



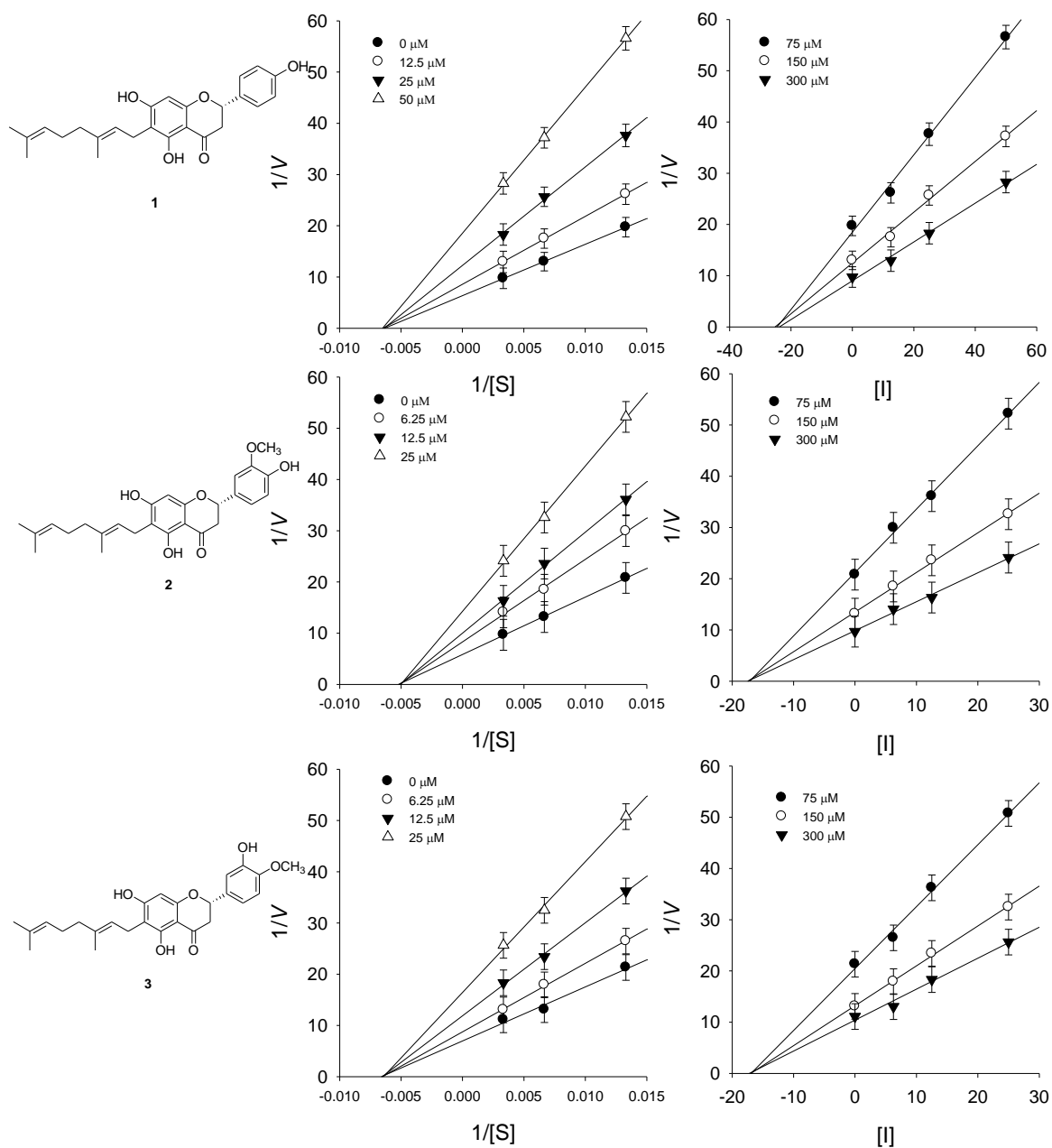
**Figure 37.** CD spectrum of compounds 1-8.



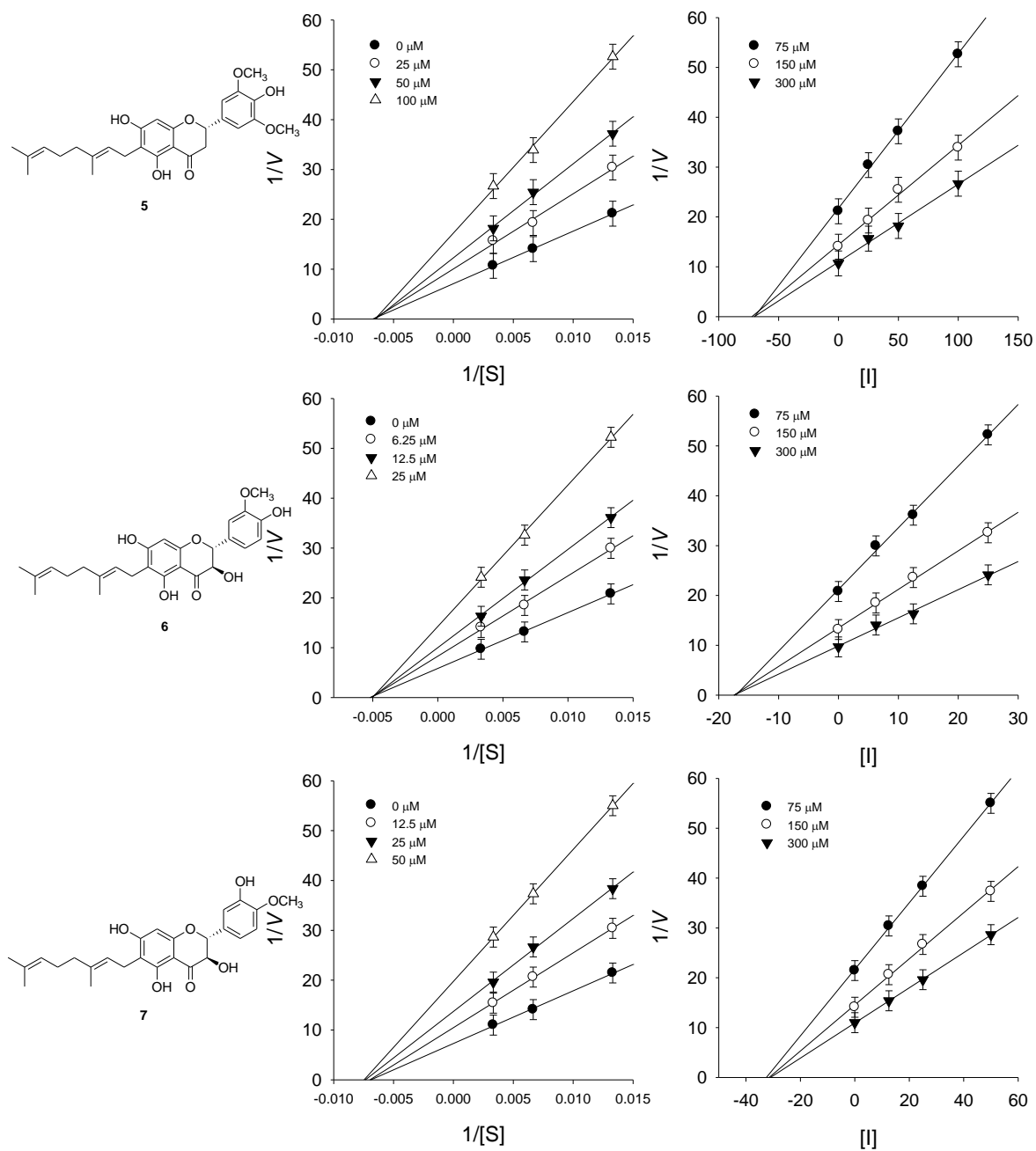
**Figure 38.** Lineweaver-Burk plots for the inhibition of PTP1B activities by compound 2-4 (left). Dixon plots for the inhibition of compounds 2-4 (right).



**Figure 39.** Lineweaver-Burk plots for the inhibition of PTP1B activities by compound 5, 7, 8 (left). Dixon plots for the inhibition of compounds 5, 7, 8 (right).



**Figure 40.** Lineweaver-Burk plots for the inhibition of  $\alpha$ -glucosidase activities by compound 1-3 (left). Dixon plots for the inhibition of compounds 1-3 (right).



**Figure 41.** Lineweaver-Burk plots for the inhibition of  $\alpha$ -glucosidase activities by compound 5-7 (left). Dixon plots for the inhibition of compounds 5-7 (right).

**Table 1.** Inhibitory effect of isolated compounds **1–8** on PTP1B.

Compounds	IC <sub>50</sub> value ( $\mu$ M)	Inhibition mode	K <sub>I</sub> ( $\mu$ M)	K <sub>IS</sub> ( $\mu$ M)
<b>1</b>	1.9 $\pm$ 0.1	Mixed Type I	0.4 $\pm$ 0.06	2.2 $\pm$ 0.1
<b>2</b>	3.9 $\pm$ 0.3	Mixed Type I	2.6 $\pm$ 0.1	3.7 $\pm$ 0.2
<b>3</b>	7.8 $\pm$ 0.6	Mixed Type I	5.7 $\pm$ 0.3	10.1 $\pm$ 0.4
<b>4</b>	5.9 $\pm$ 0.4	Mixed Type I	5.5 $\pm$ 0.3	11.2 $\pm$ 0.4
<b>5</b>	3.8 $\pm$ 0.3	Mixed Type I	2.8 $\pm$ 0.2	4.6 $\pm$ 0.2
<b>6</b>	4.9 $\pm$ 0.5	Mixed Type I	3.5 $\pm$ 0.2	5.2 $\pm$ 0.2
<b>7</b>	8.2 $\pm$ 0.6	Mixed Type I	6.9 $\pm$ 0.4	13.7 $\pm$ 0.6
<b>8</b>	6.6 $\pm$ 0.5	Mixed Type I	5.9 $\pm$ 0.3	10.3 $\pm$ 0.5