

Supporting Information

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Pterosterone 20,22-Acetonide, a New Ecdysteroid and Other Constituents from *Acrostichum aureum* L.

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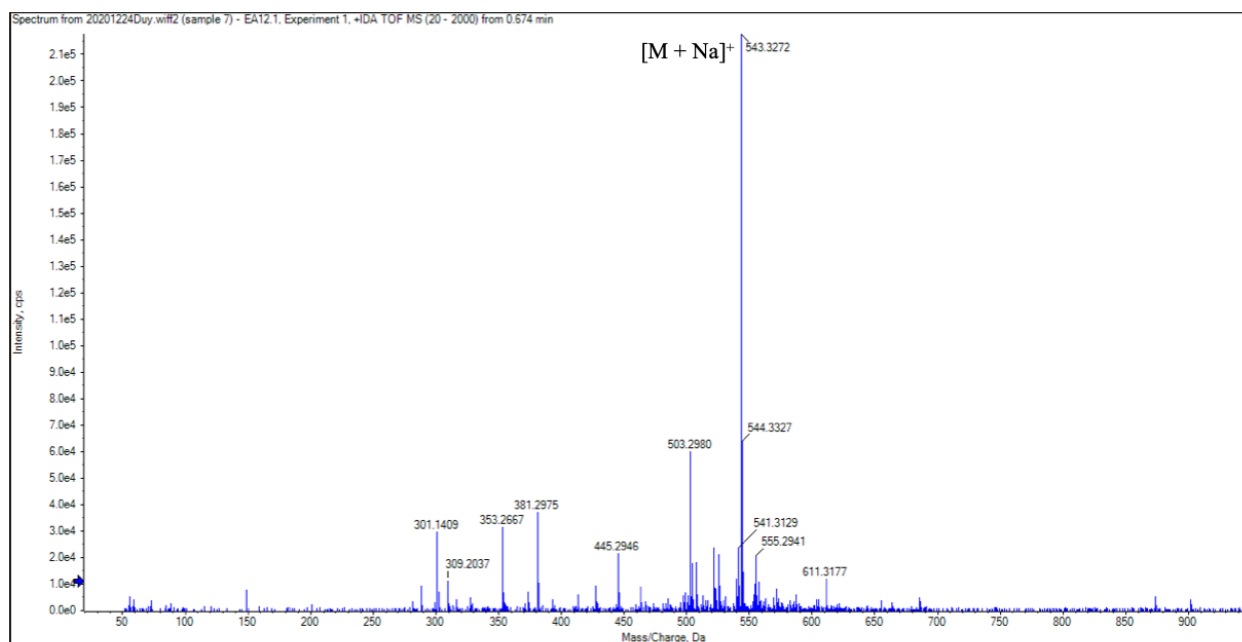


Figure S1: HR-ESI Mass Spectrum of Pterosterone 20,22-acetonide (**1**)

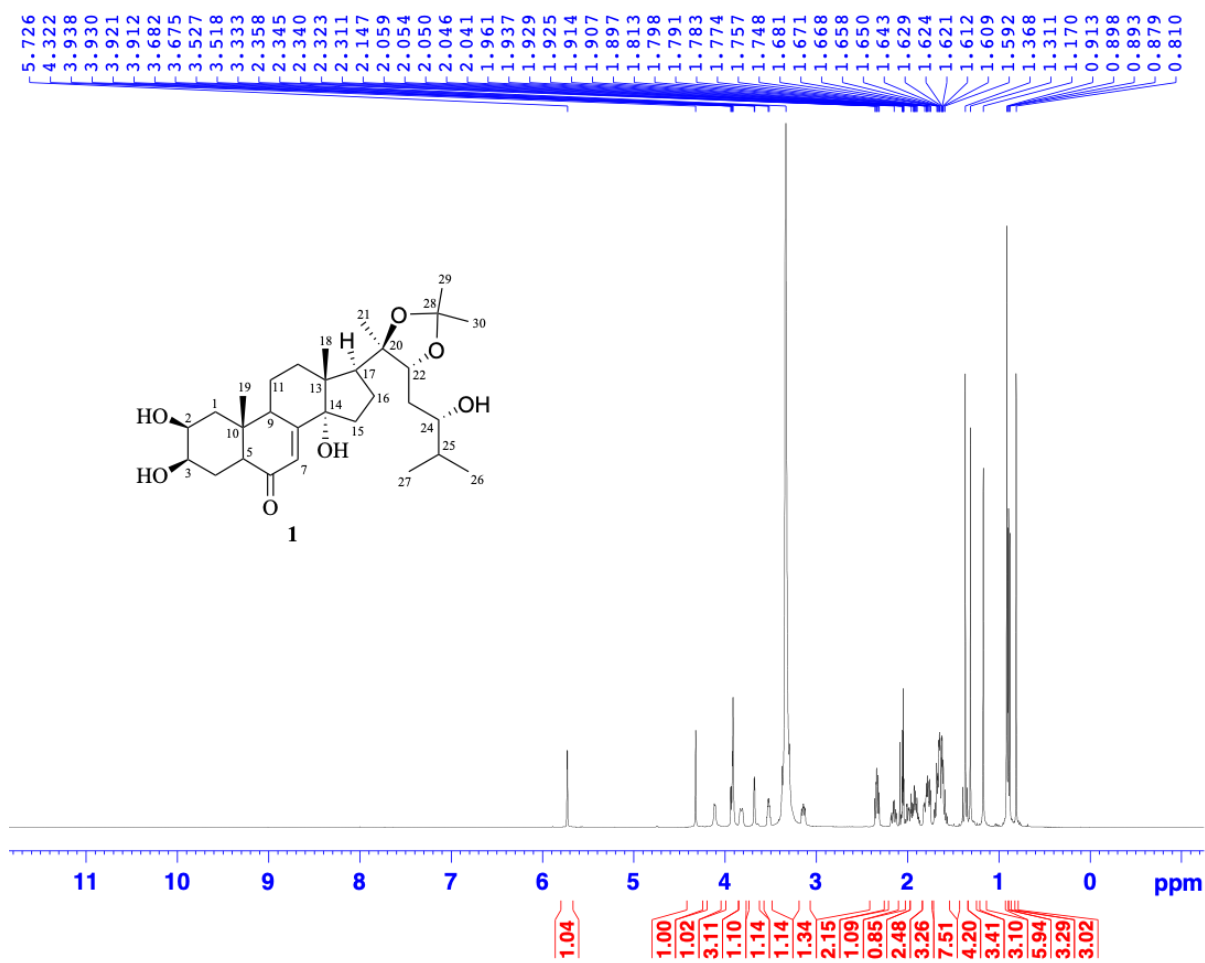


Figure S2: ¹H-NMR (500 MHz, acetone-*d*₆) Spectrum of Pterosterone 20,22-acetonide (**1**)

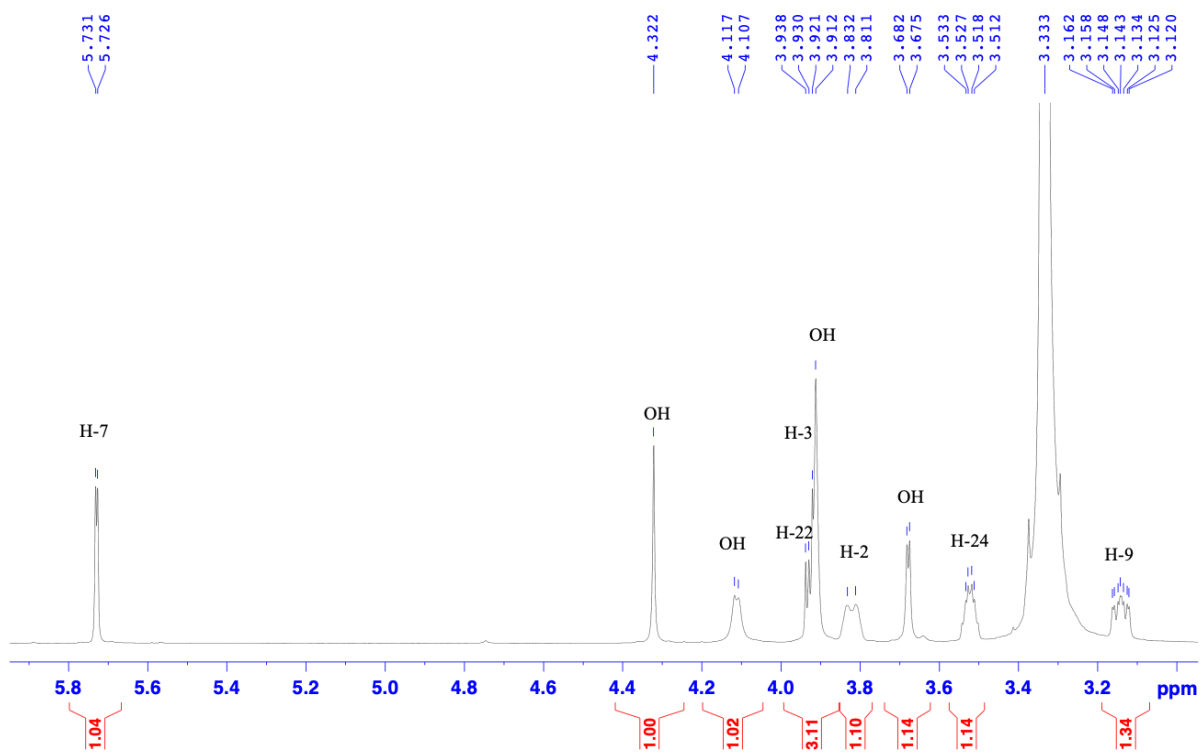


Figure S3: $^1\text{H-NMR}$ (500 MHz, acetone- d_6) Spectrum of **1** (from δ_{H} 3.0 ppm to 6.0 ppm)

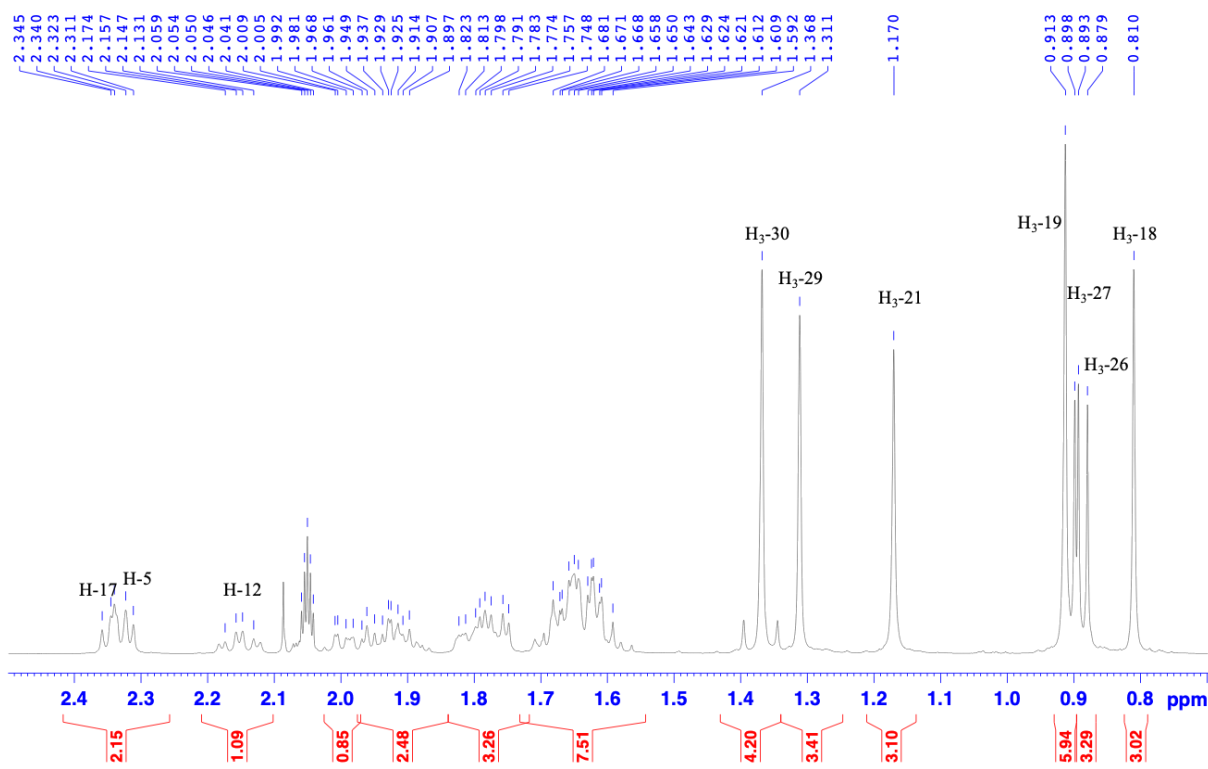


Figure S4: $^1\text{H-NMR}$ (500 MHz, acetone- d_6) Spectrum of **1** (from δ_{H} 0.5 ppm to 2.4 ppm)

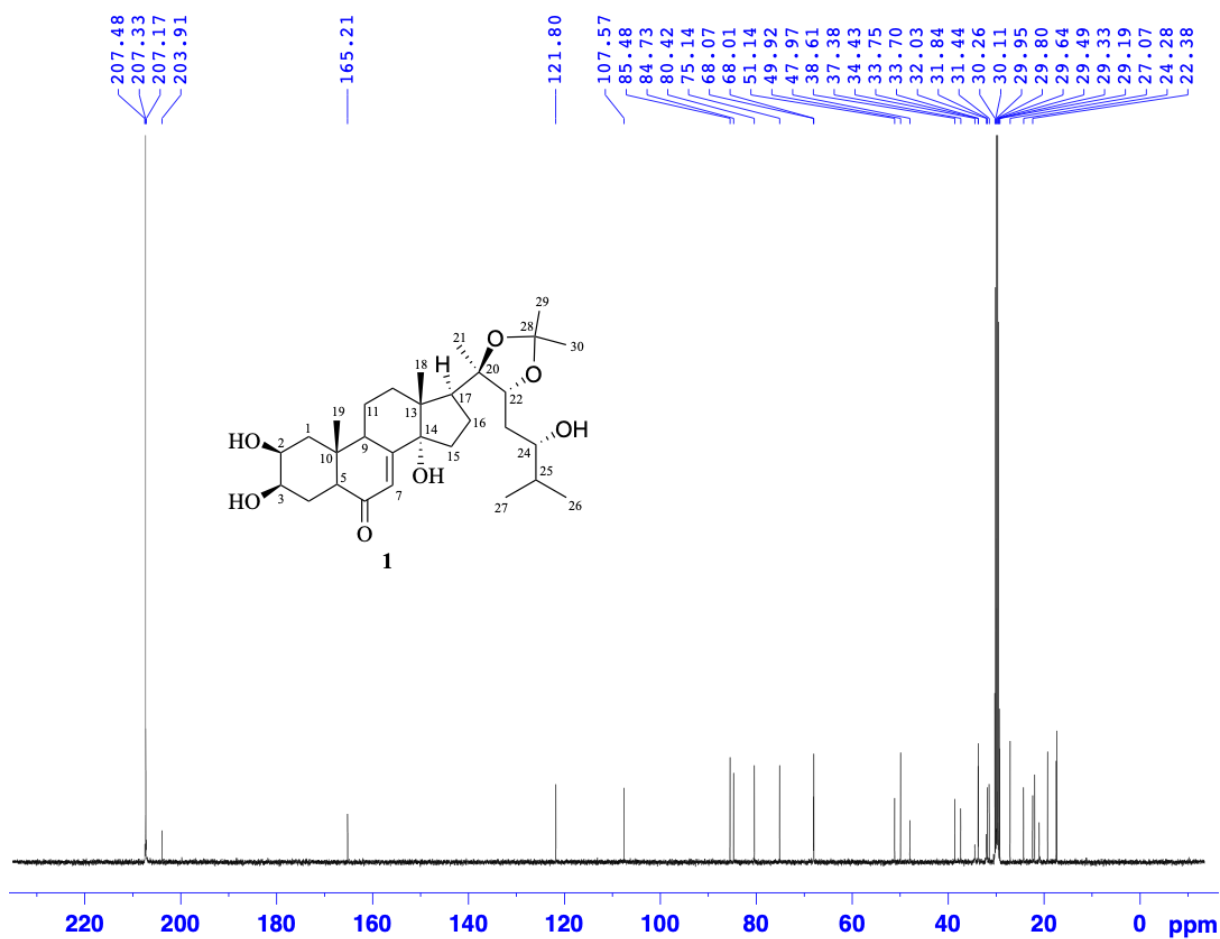


Figure S5: ^{13}C -NMR (125 MHz, acetone- d_6) Spectrum of Pterosterone 20,22-acetonide (**1**)

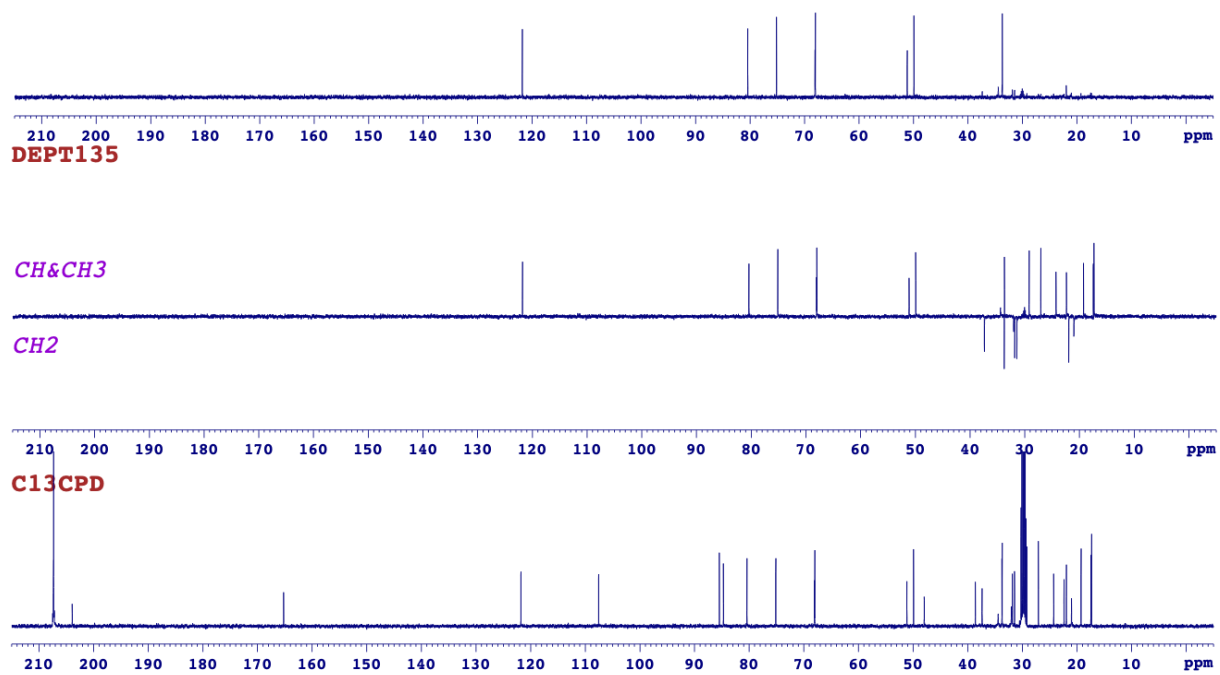


Figure S6: DEPT 90 and 135 (125 MHz, acetone- d_6) Spectrum of **1**

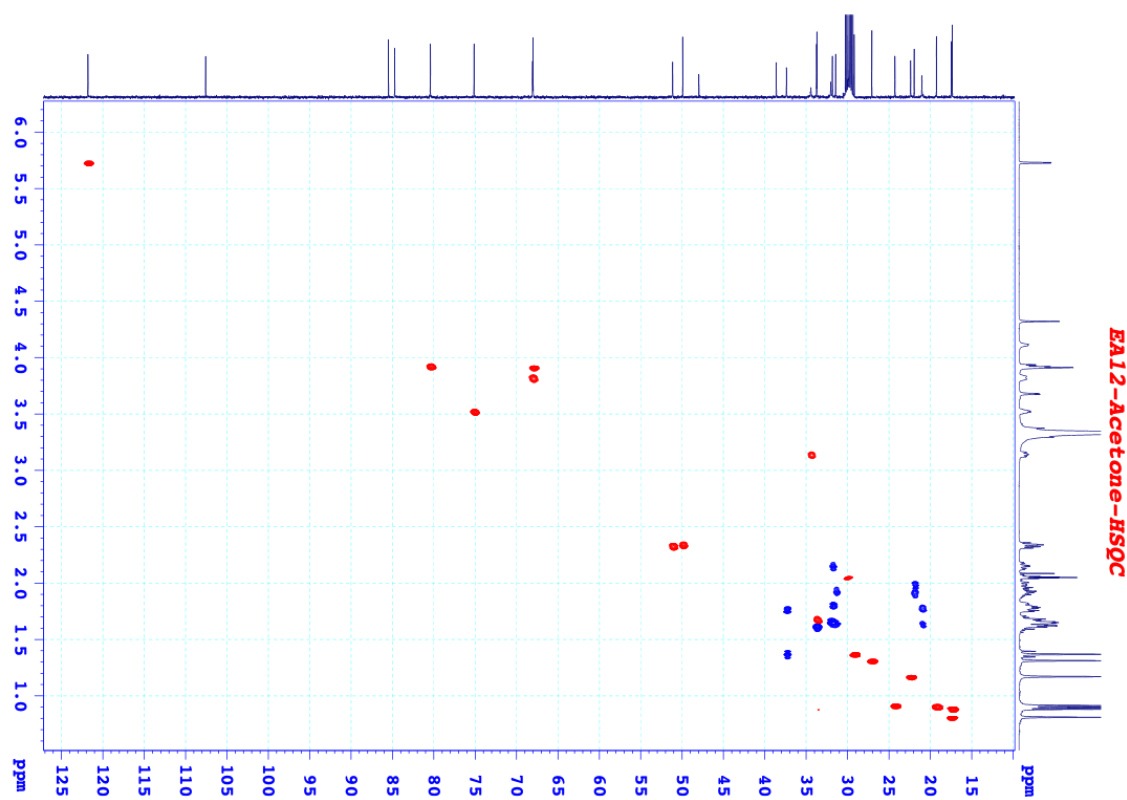


Figure S7: HSQC Spectrum of Pterosterone 20,22-acetonide (**1**)

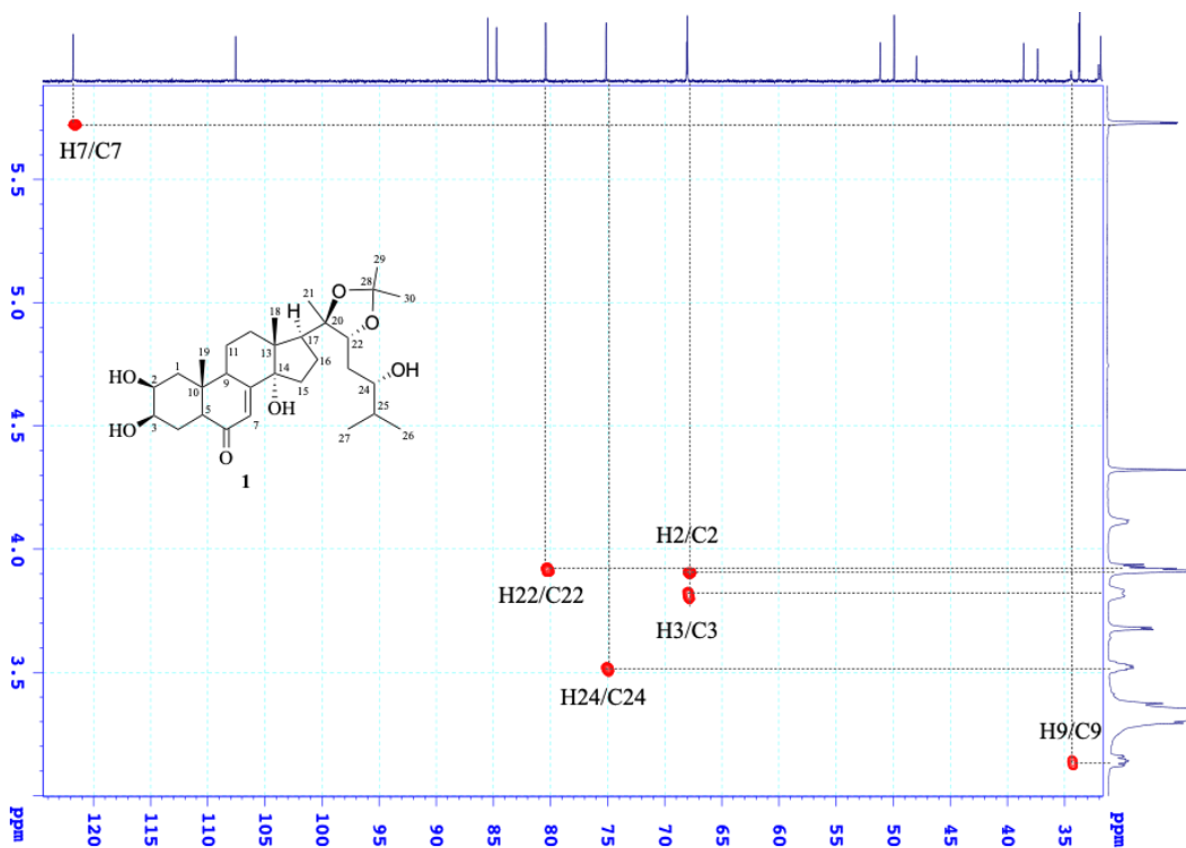


Figure S8: HSQC Spectrum of **1** (from δ_c 30 ppm to δ_c 125 ppm)

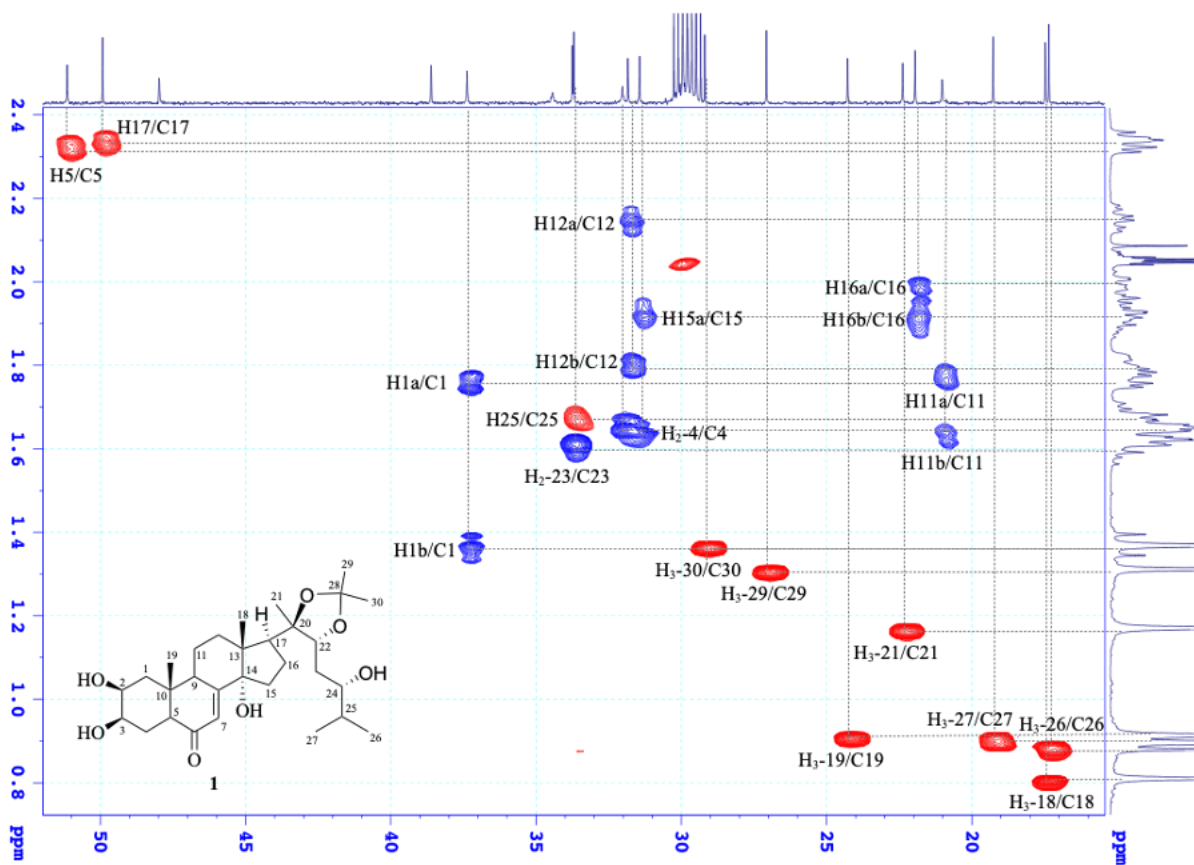


Figure S9: HSQC Spectrum of **1** (from δ_c 15 ppm to δ_c 55 ppm)

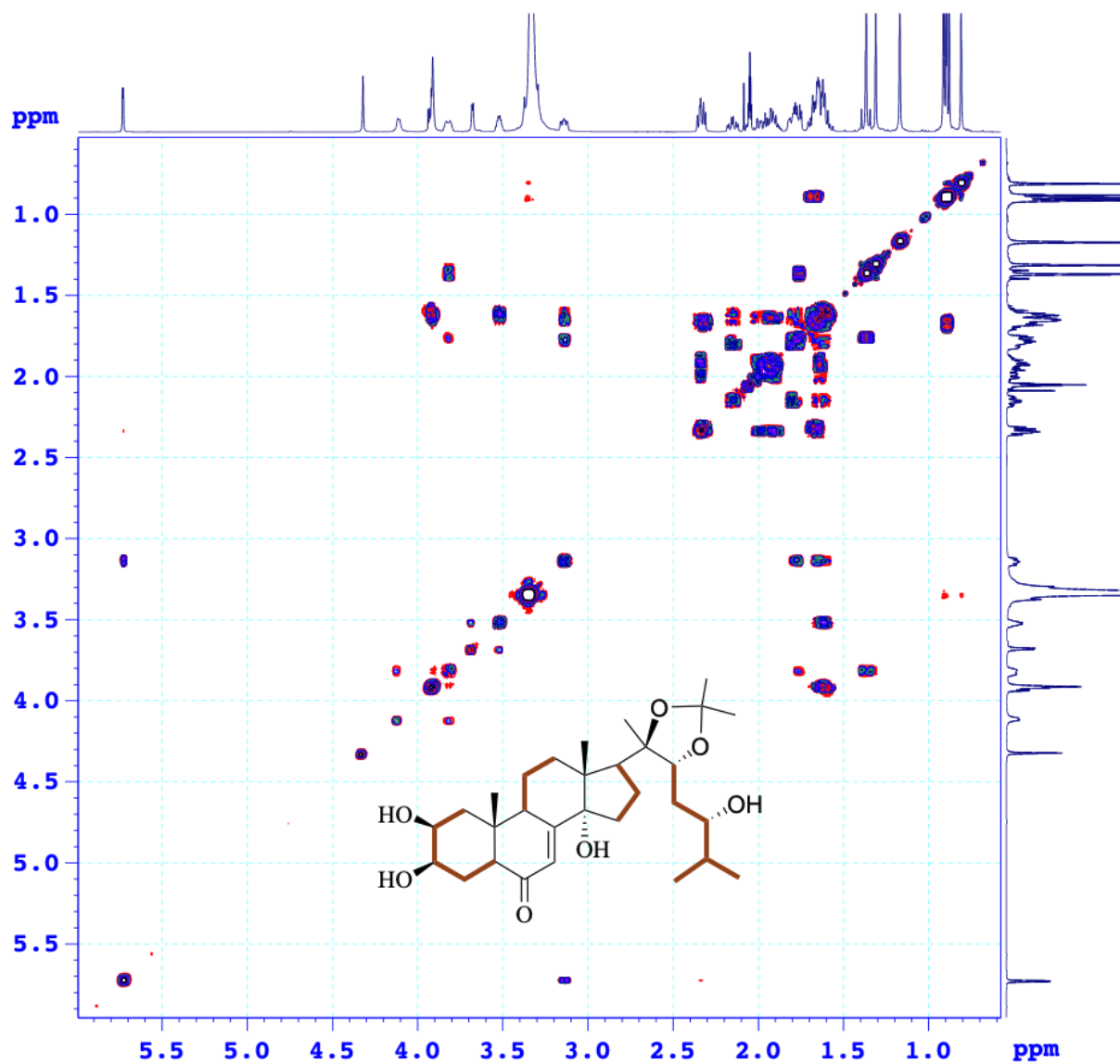


Figure S10: ^1H - ^1H COSY Spectrum of Pterosterone 20,22-acetonide (1)

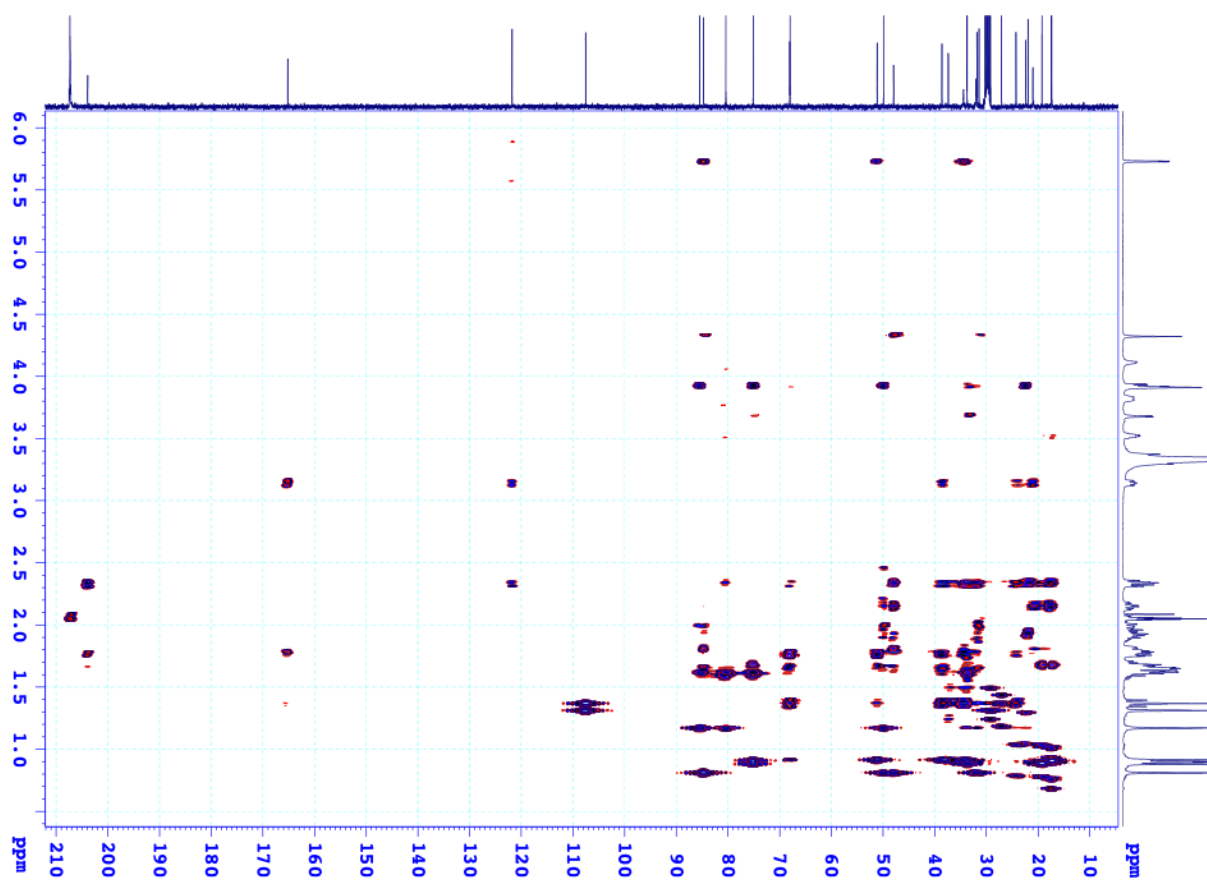


Figure S11: HMBC Spectrum of Pterosterone 20,22-acetonide (**1**)

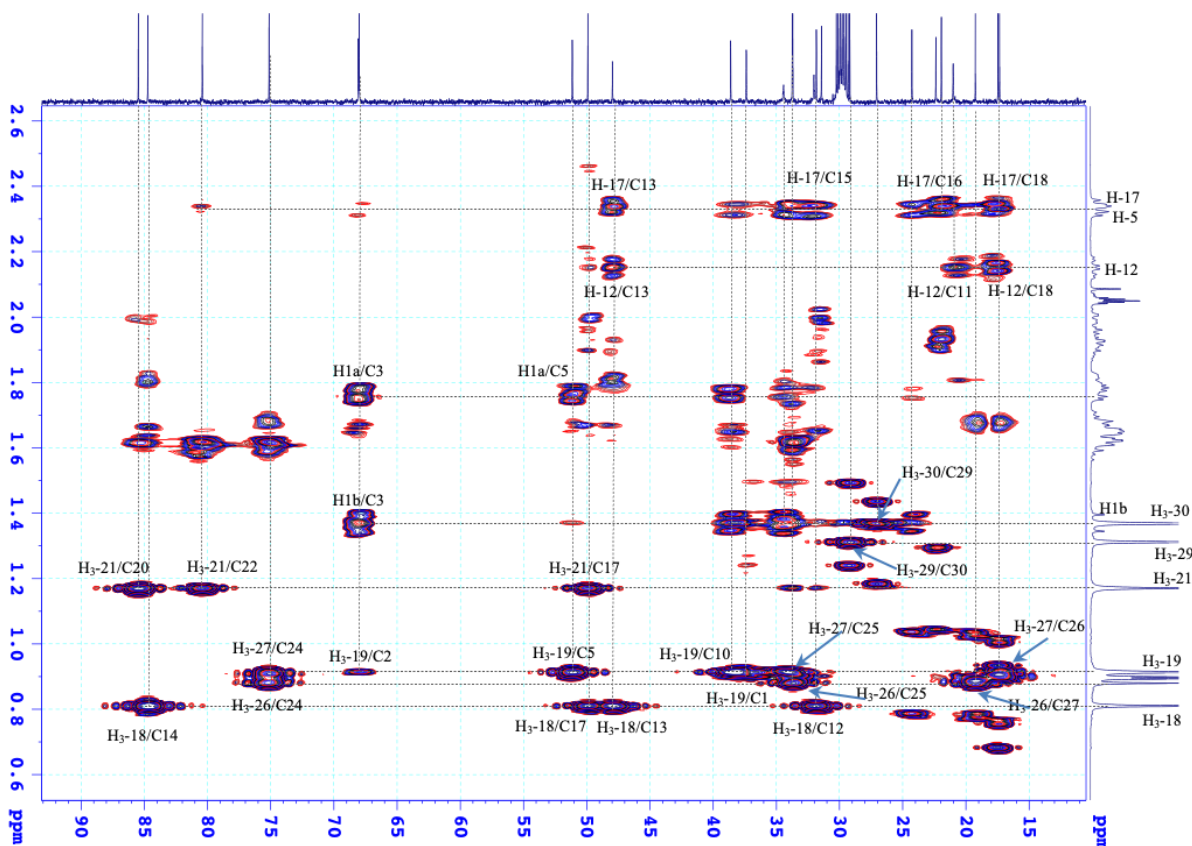
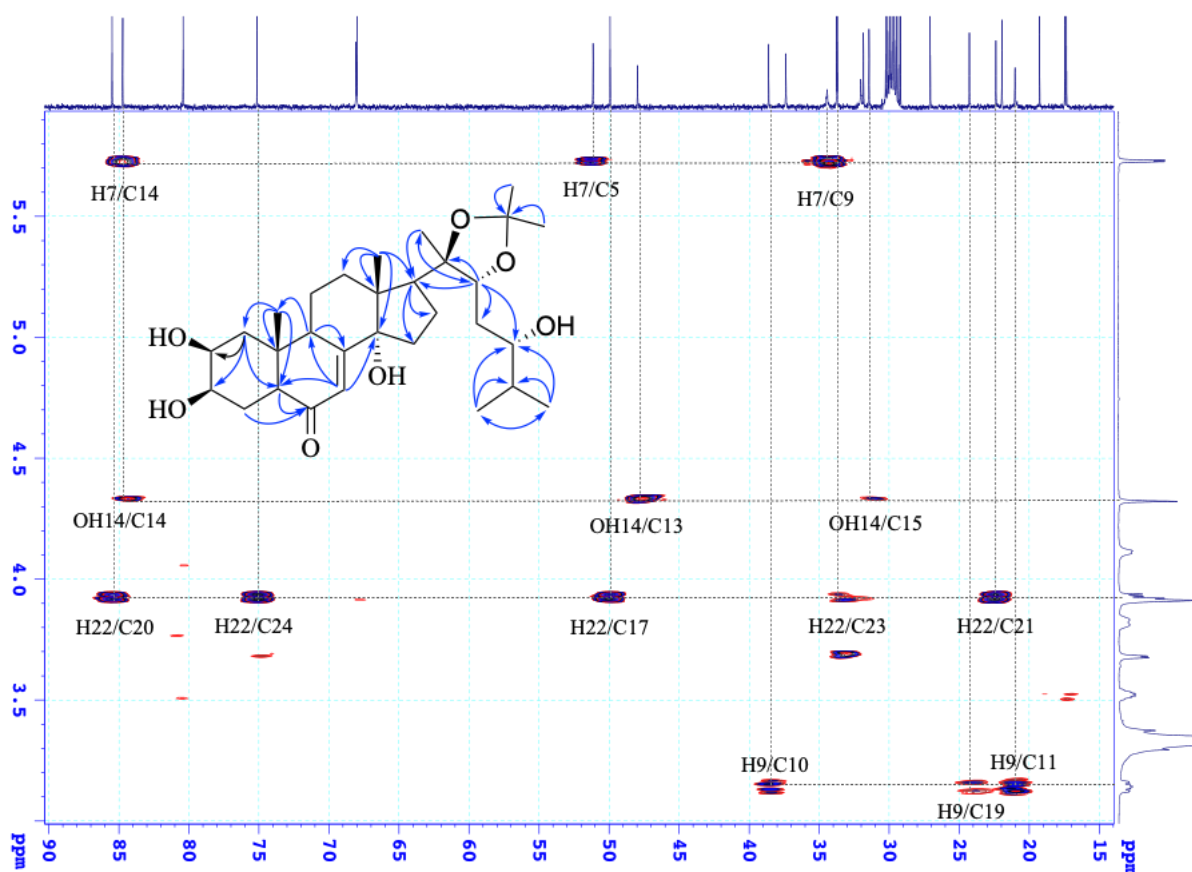


Figure S12: HMBC Spectrum of 1 (From δ_c 15 ppm to δ_c 90 ppm)

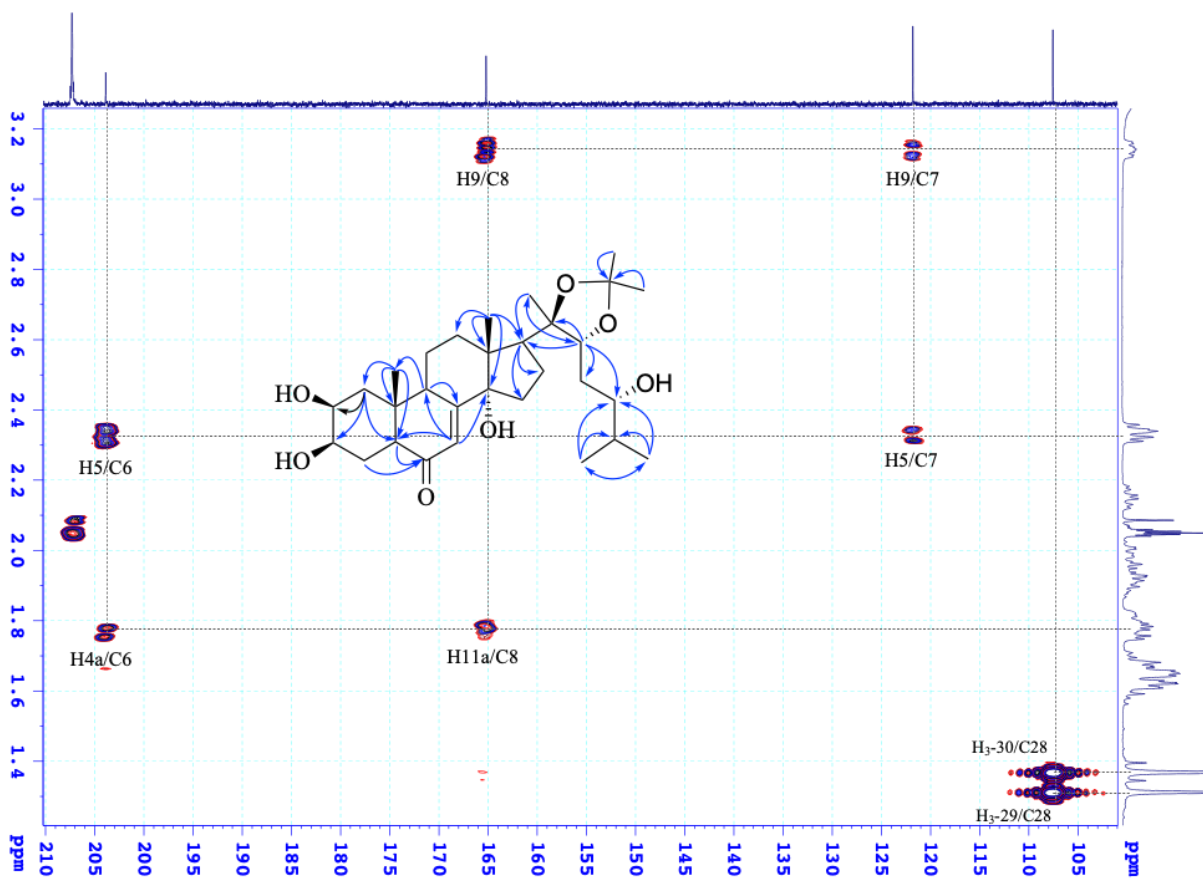


Figure S13: HMBC Spectrum of **1** (From δ_c 105 ppm to δ_c 210 ppm)

EA12-AcetoneD6-NOESY

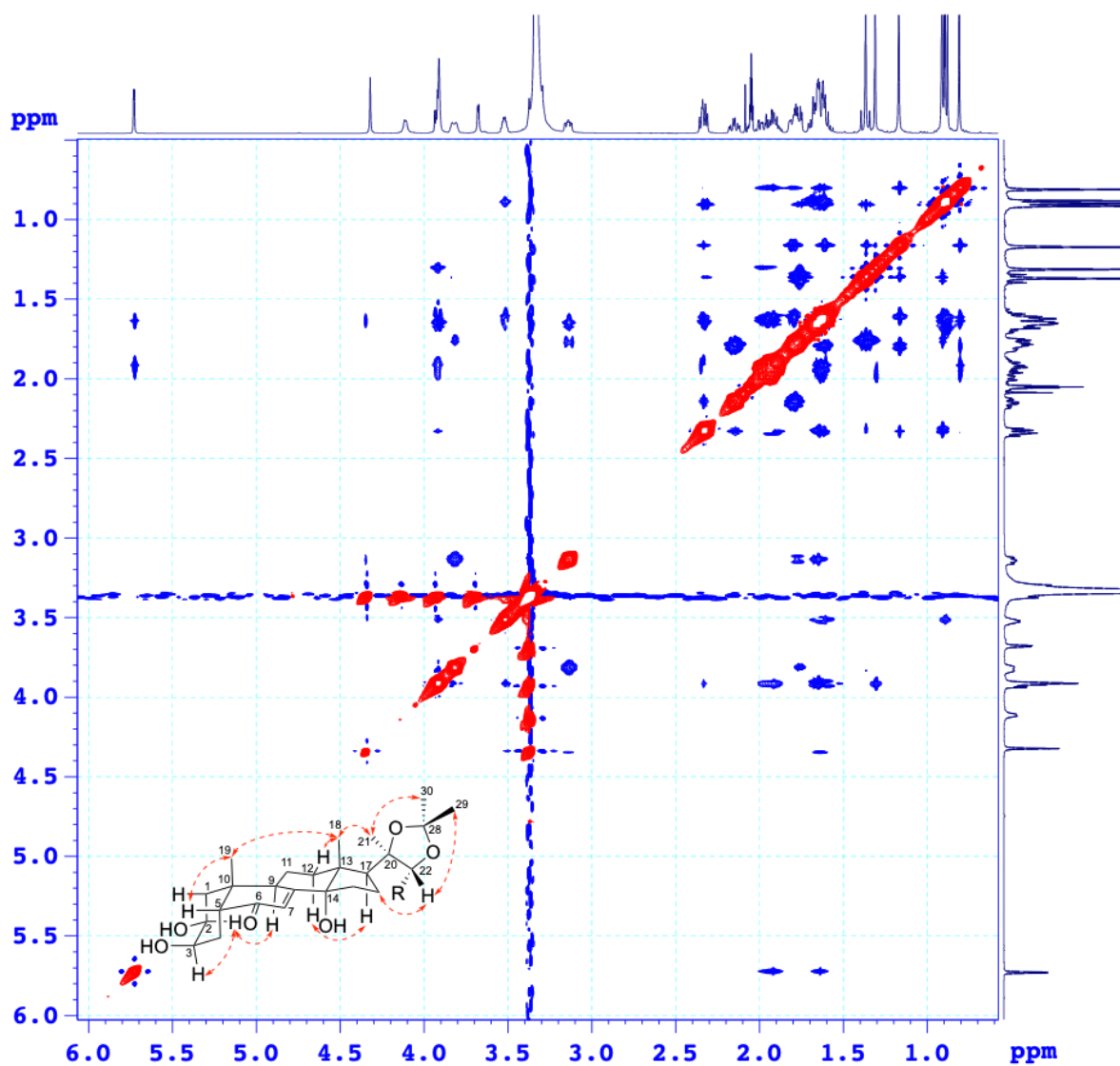


Figure S14: NOESY Spectrum of Pterosterone 20,22-acetonide (1)

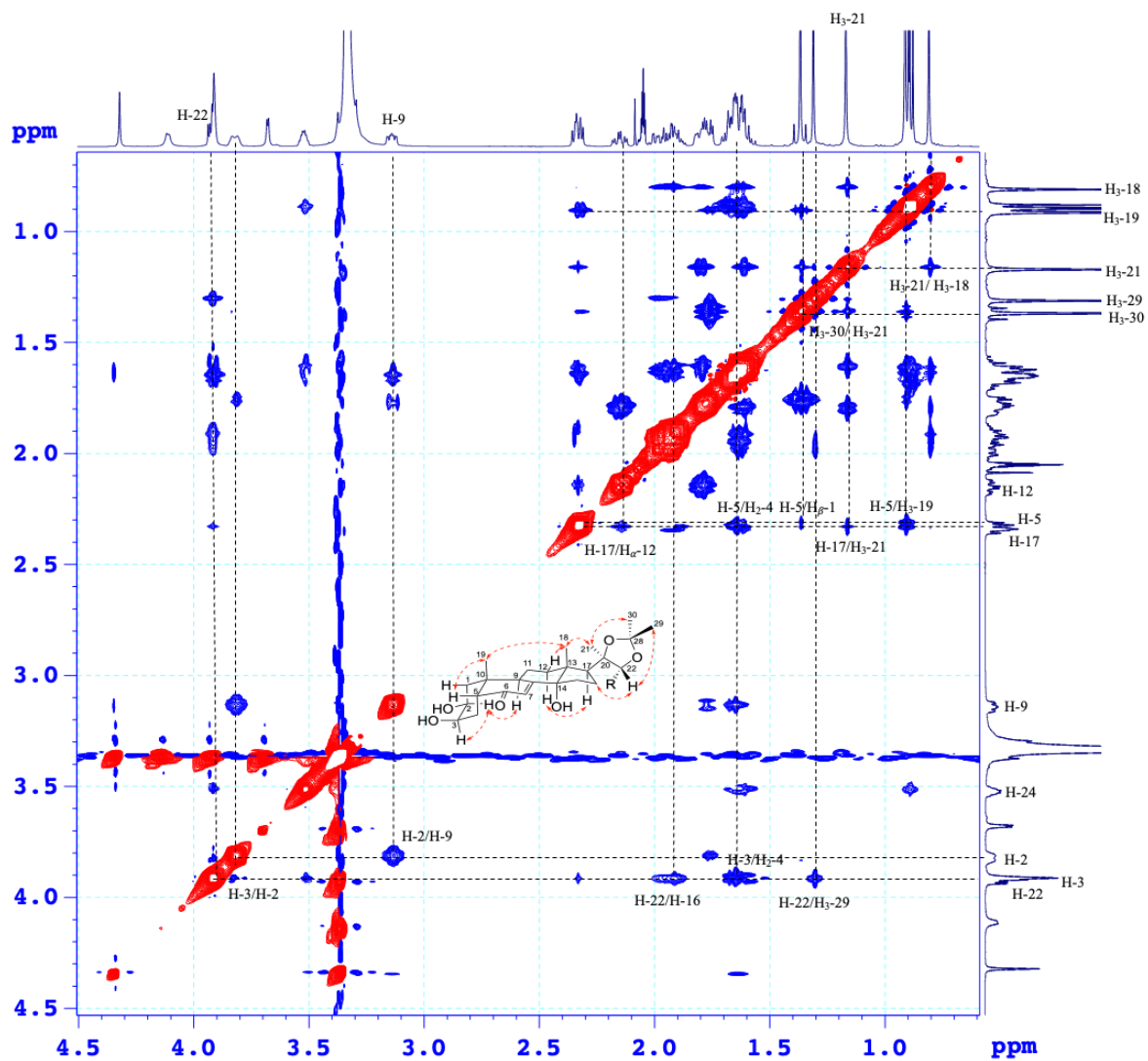


Figure S15: NOESY Spectrum of 1 (Expansion)

Initiating Search

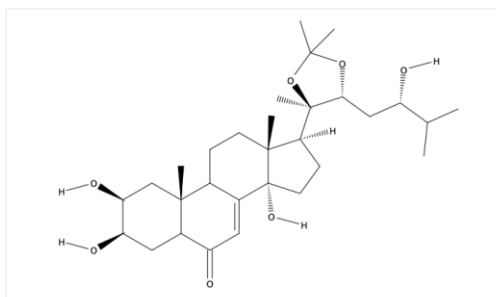
April 12, 2023, 6:10PM

Substances:

Filtered By:

Similarity: 95-98

Number of Components: 1



Structure Match: Similarity

Search Tasks

| Task | Search Type | View |
|---|-------------|------------------------------|
| Exported: Returned Substance Results + Filters (47) | Substances | View Results |

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CAS SciFinder® Substances Enter a query... Edit

Substances search for drawn structure

References Reactions Suppliers

Structure Match: As Drawn (0), Substructure (1), Similarity (385K)

Chemscape Analysis: Visually explore structure similarity with a powerful new tool. [Learn more about Chemscape.](#) [Create Chemscape Analysis](#)

Filter Behavior: Filter by Exclude

Search Within Results: Similarity (95-98 (47) selected, 90-94 (123), 85-89 (308), 80-84 (1,463), 75-79 (7,697), View All)

Filtering: Similarity: 95-98 X Number of Components: Edit Drawing Remove Clear All Filters

47 Results

| | | |
|---|---|--|
| <p>1 98</p> <p>22798-96-5</p> <p>Absolute stereochemistry shown, Rotation (+)</p> <p>$C_{30}H_{48}O_7$ 20-Hydroxyecdysone 20,22-acetonide</p> <p>75 References 53 Reactions 19 Suppliers</p> | <p>2 98</p> <p>84507-68-6</p> <p>Absolute stereochemistry shown</p> <p>$C_{30}H_{48}O_7$ Cholest-7-en-6-one, 2,3,14,25-tetrahydroxy-20,22-[[1-methylethylidene]bis(oxy)]...</p> <p>4 References 0 Reactions 0 Suppliers</p> | <p>3 98</p> <p>802985-96-2</p> <p>Absolute stereochemistry shown, Rotation (+)</p> <p>$C_{31}H_{50}O_7$ (2β,3β,5β,22β)-2,3,14,25-Tetrahydroxy-20,22-[[1β-(1-methylpropylidene)bis(oxy)]...</p> <p>2 References 2 Reactions 0 Suppliers</p> |
| <p>4 98</p> <p>698975-67-6</p> <p>Absolute stereochemistry shown</p> <p>$C_{30}H_{48}O_7$ (2α,3α,5β,22β)-2,3,14,25-Tetrahydroxy-20,22-[[1-methylethylidene]bis(oxy)]</p> | <p>5 98</p> <p>1637251-65-0</p> <p>Absolute stereochemistry shown</p> <p>$C_{32}H_{52}O_7$ (2β,3β,5β,22β)-20,22-[[1-Ethylpropylidene]bis(oxy)]-2,3,14,25-tetrahydroxy-</p> | <p>6 98</p> <p>698975-70-1</p> <p>Absolute stereochemistry shown</p> <p>$C_{30}H_{48}O_7$ Cholest-7-en-6-one, 2,3,14,25-tetrahydroxy-20,22-[[1-methylethylidene]bis(oxy)]...</p> |

Figure S15: SciFinder Search Results of Compound 1

Ponasterone A 20,22-acetonide (2): ^1H NMR (500 MHz, acetone- d_6) data (Table S1); ^{13}C NMR (125 MHz, acetone- d_6) data (Table S2).

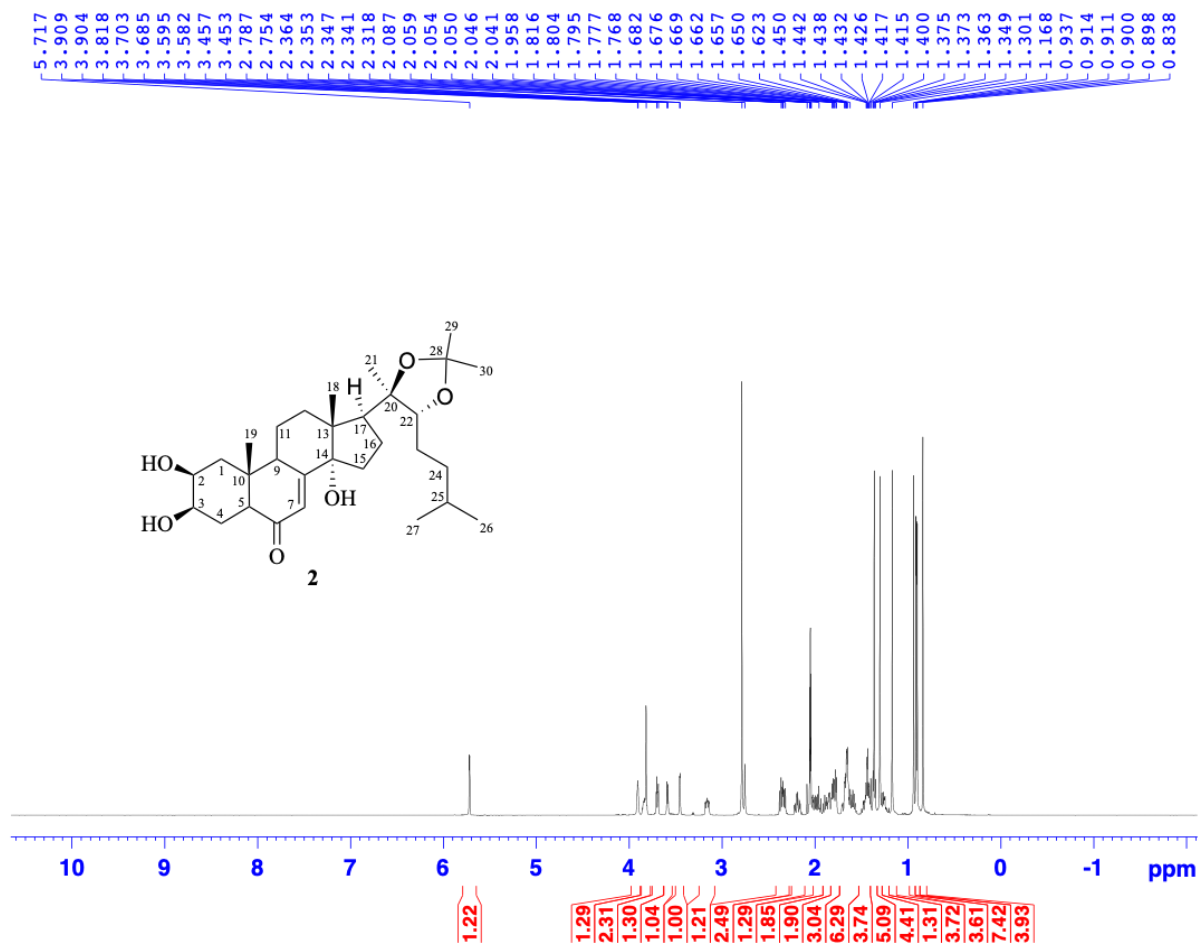


Figure S16: ^1H -NMR (500 MHz, acetone- d_6) Spectrum of Ponasterone A 20, 22-acetonide (2)

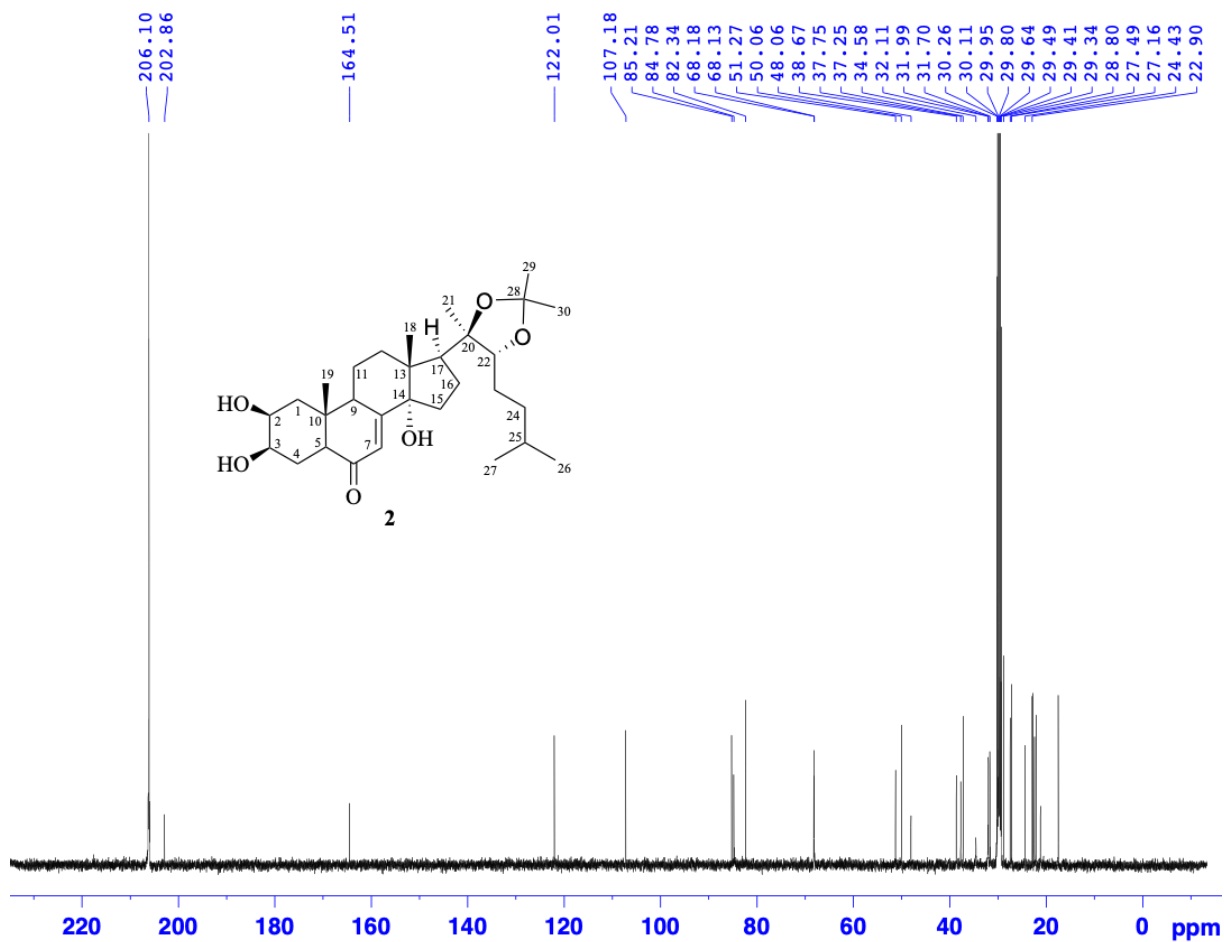


Figure S17: ^{13}C -NMR (125 MHz, acetone- d_6) Spectrum of Ponasterone A 20, 22-acetonide (**2**)

Pterosterone (3): ^1H NMR (500 MHz, CD_3OD) data (Table S1); ^{13}C NMR (125 MHz, CD_3OD) data (Table S2).

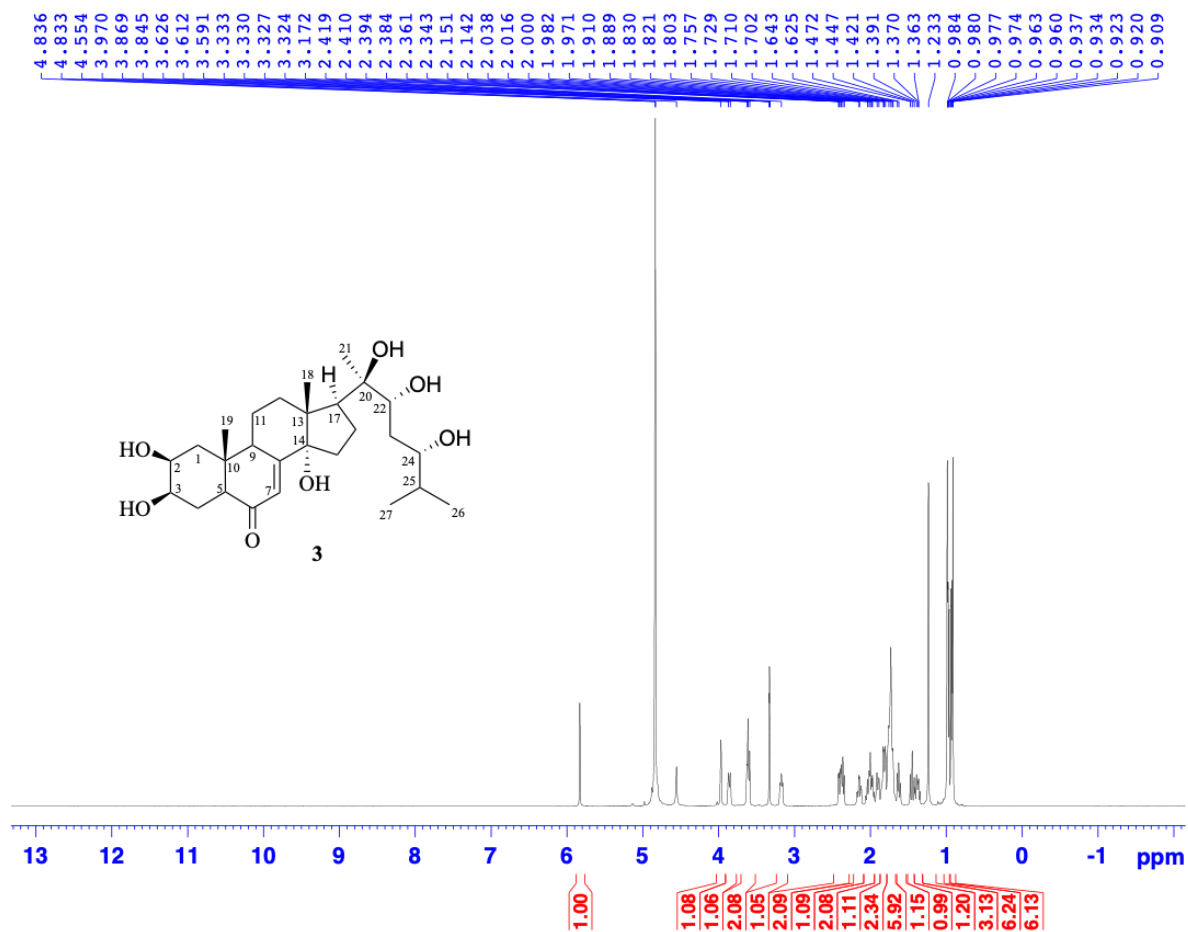


Figure S18: ^1H -NMR (500 MHz, CD_3OD) Spectrum of Pterosterone (3)

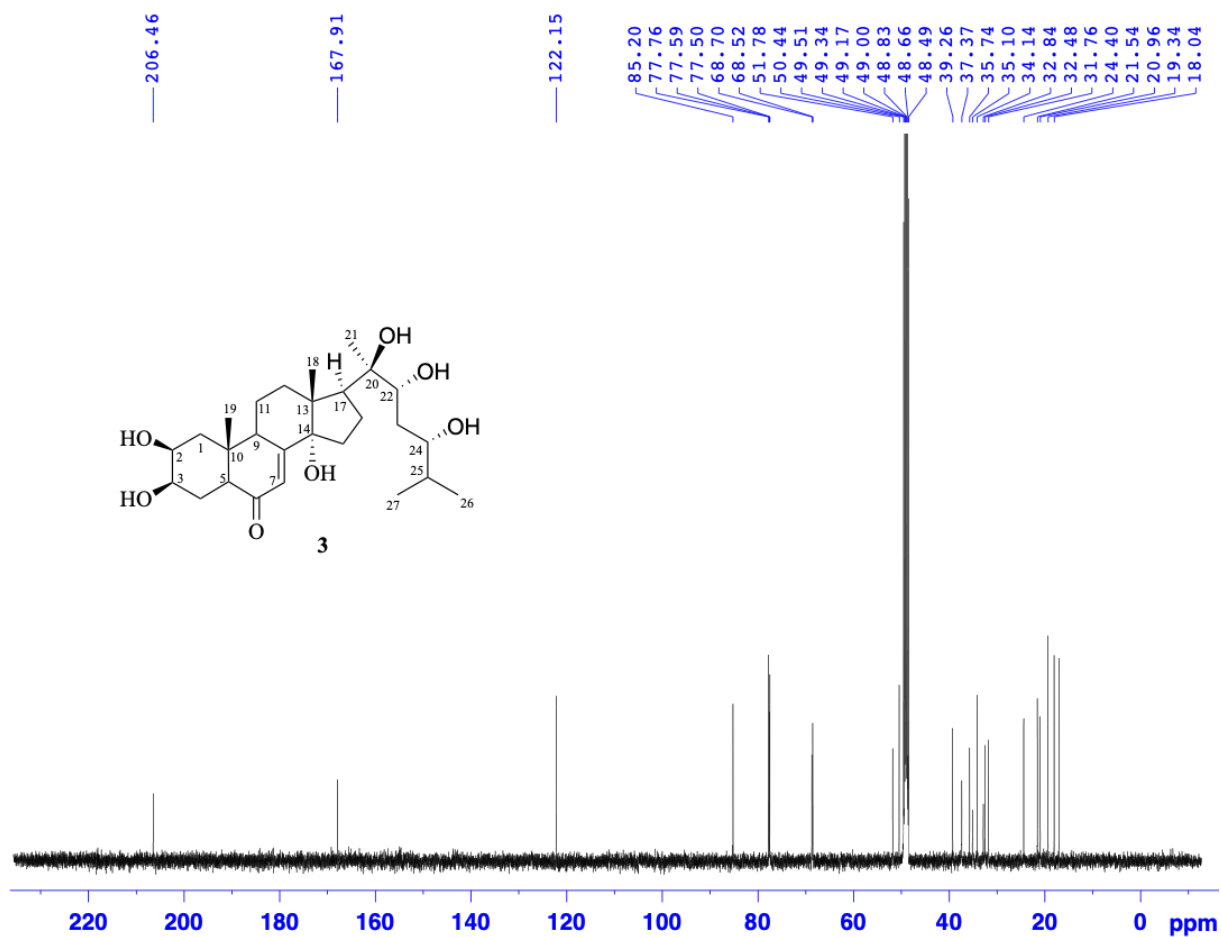


Figure S19: ¹³C-NMR (125 MHz, CD₃OD) Spectrum of Pterosterone (3)

Ponasterone A (4): ^1H NMR (500 MHz, CD_3OD) data (Table S1); ^{13}C NMR (125 MHz, CD_3OD) data (Table S2).

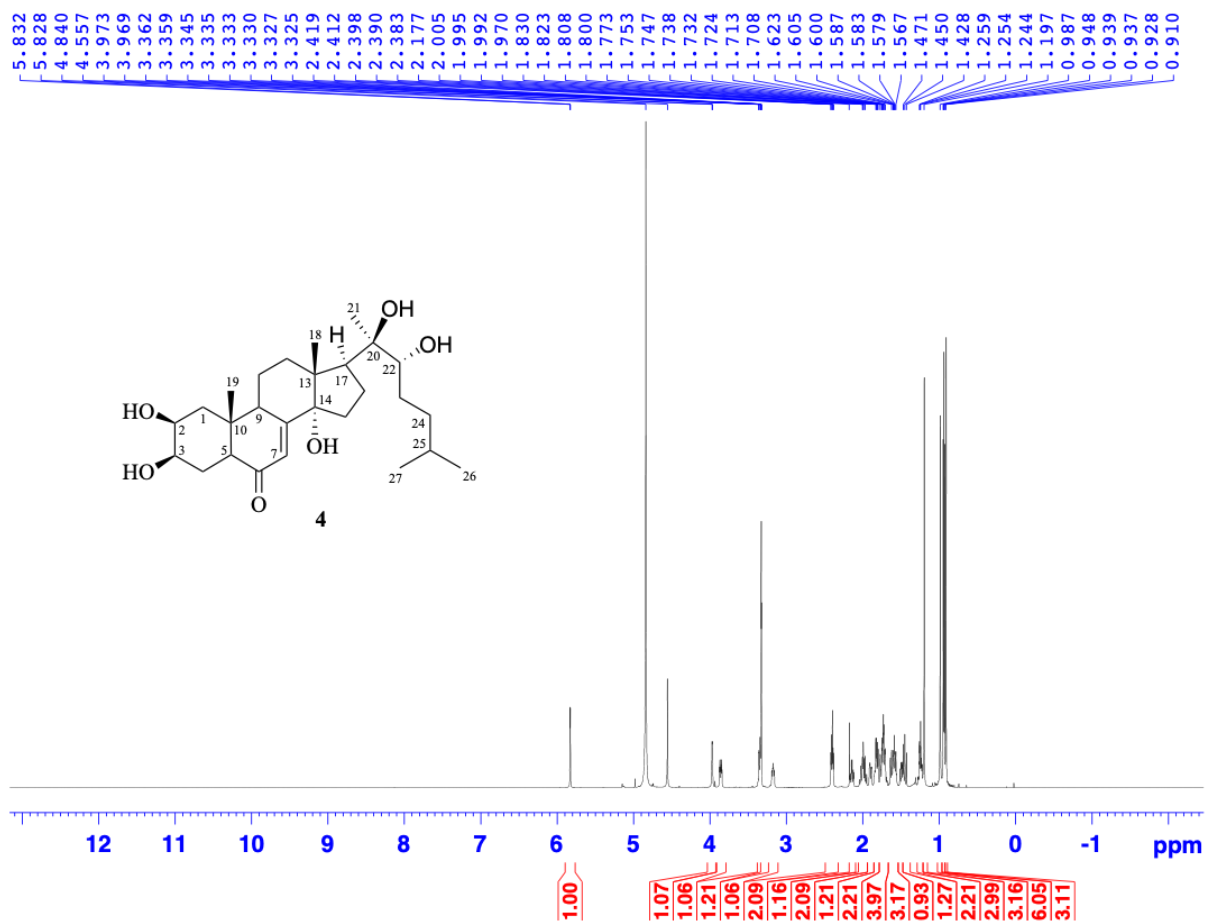


Figure S20: ^1H -NMR (500 MHz, CD_3OD) Spectrum of Ponasterone A (4)

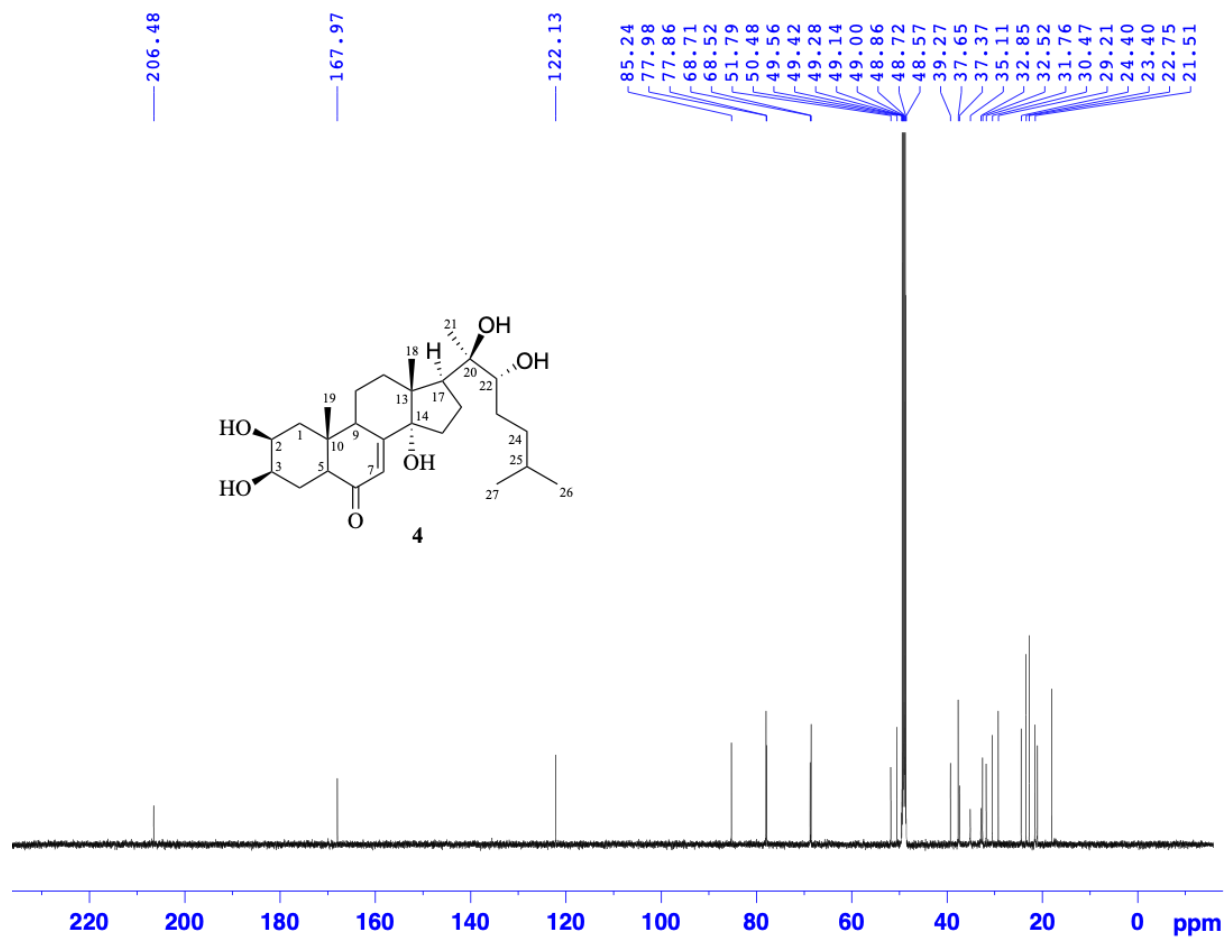


Figure S21: ¹³C-NMR (125 MHz, CD₃OD) Spectrum of Ponasterone A (4)

24-(2-Hydroxyethyl)-20-hydroxyecdysone (5): ^1H NMR (500 MHz, $\text{DMSO-}d_6$) data (Table S1); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) data (Table S2).

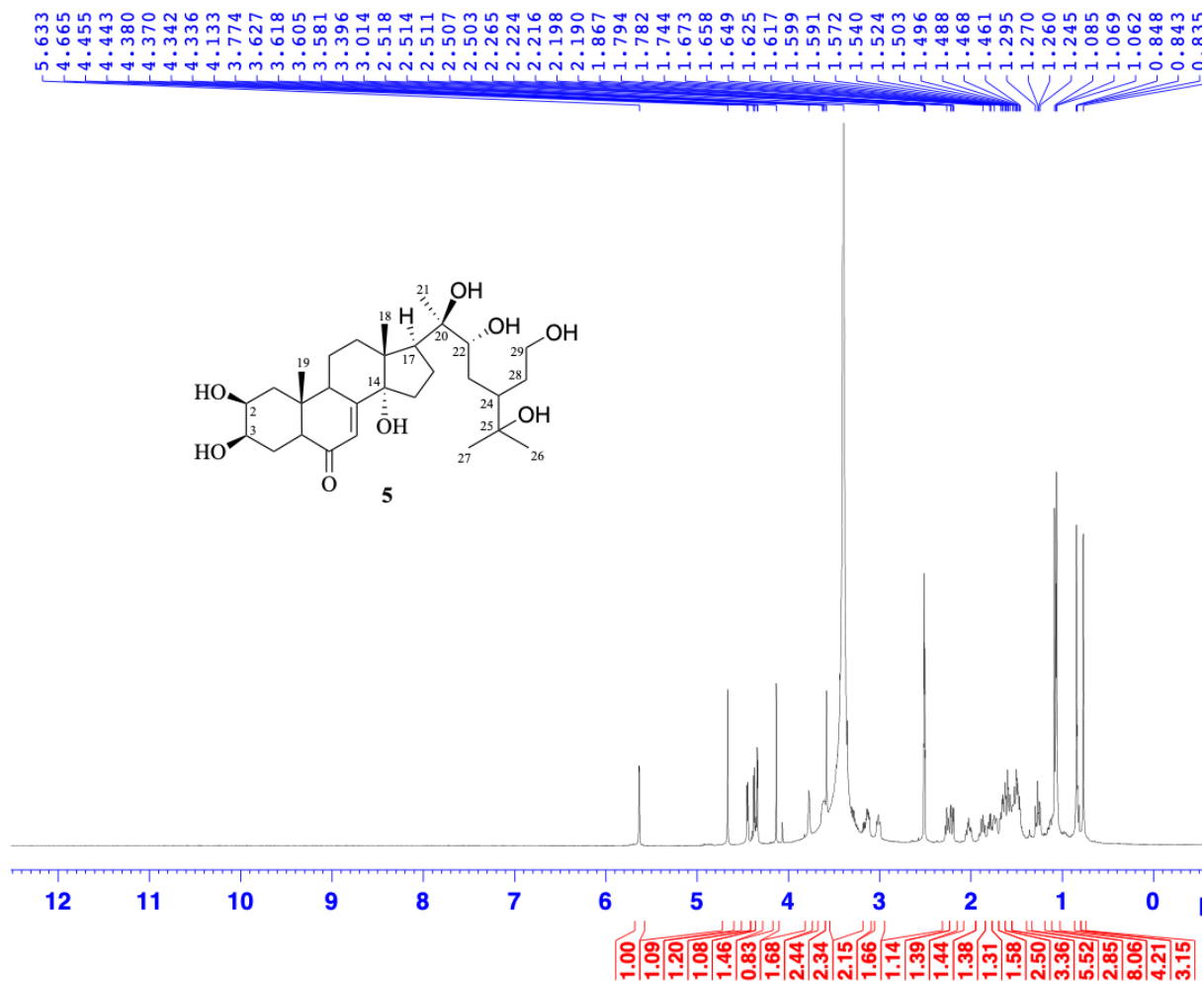


Figure S22: ^1H -NMR (500 MHz, $\text{DMSO-}d_6$) Spectrum of 24-(2-Hydroxyethyl)-20-hydroxyecdysone (5)

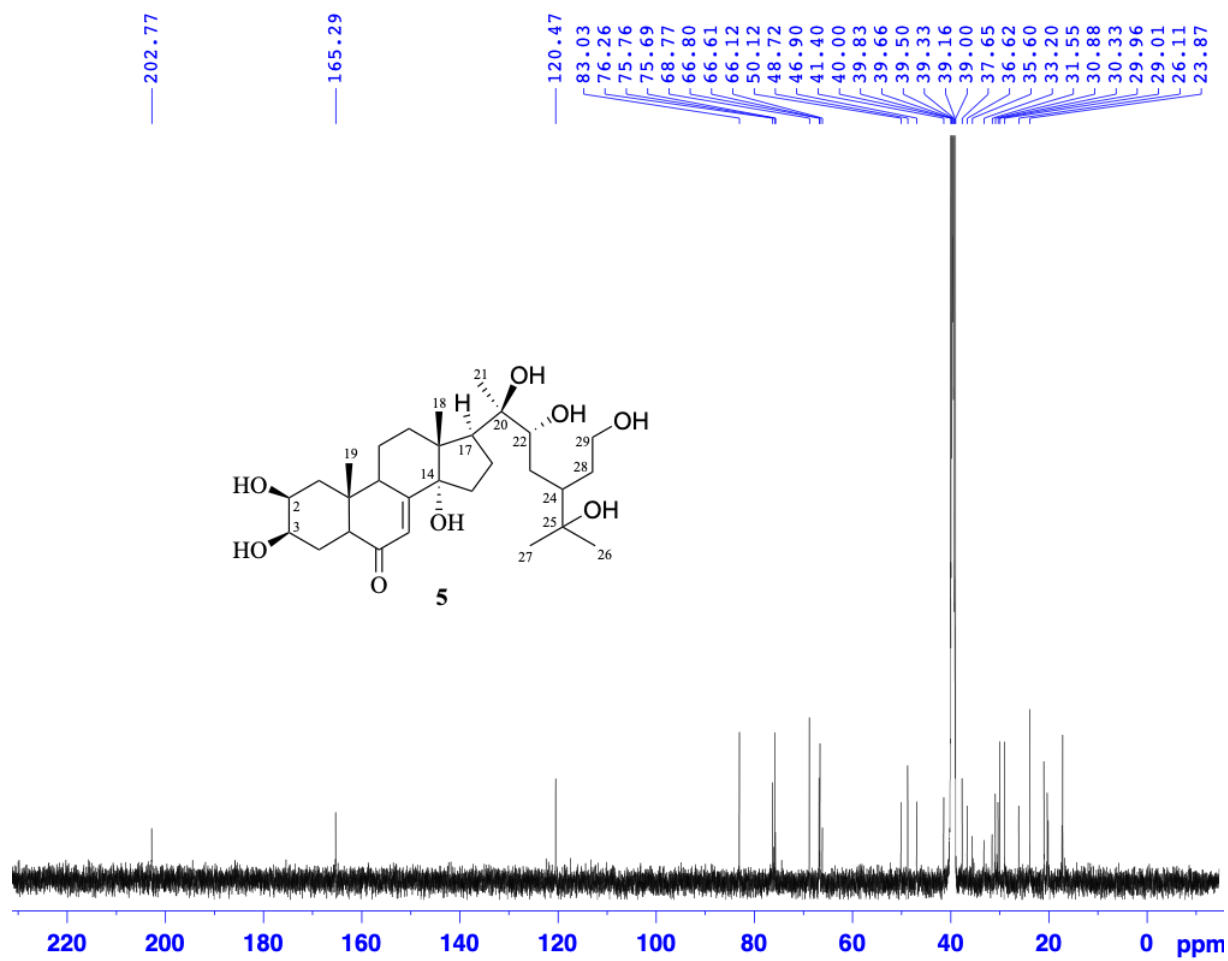


Figure S23: ^{13}C -NMR (125 MHz, $\text{DMSO-}d_6$) Spectrum of 24-(2-Hydroxyethyl)-20-hydroxyecdysone (**5**)

Quercetin (6): ^1H NMR (500 MHz, $\text{DMSO-}d_6$) data (Table S3); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) data (Table S4).

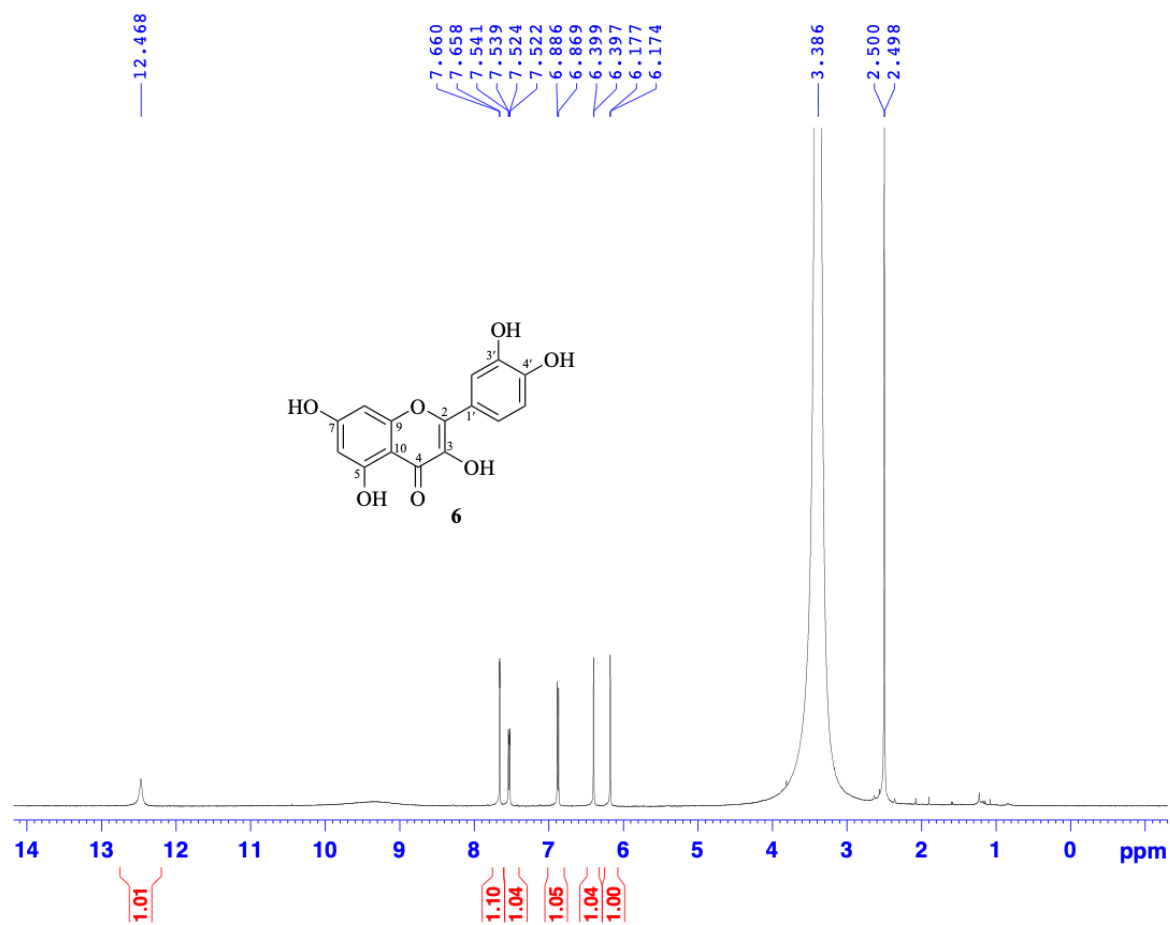


Figure S24: ^1H -NMR (500 MHz, $\text{DMSO-}d_6$) Spectrum of Quercetin (6)

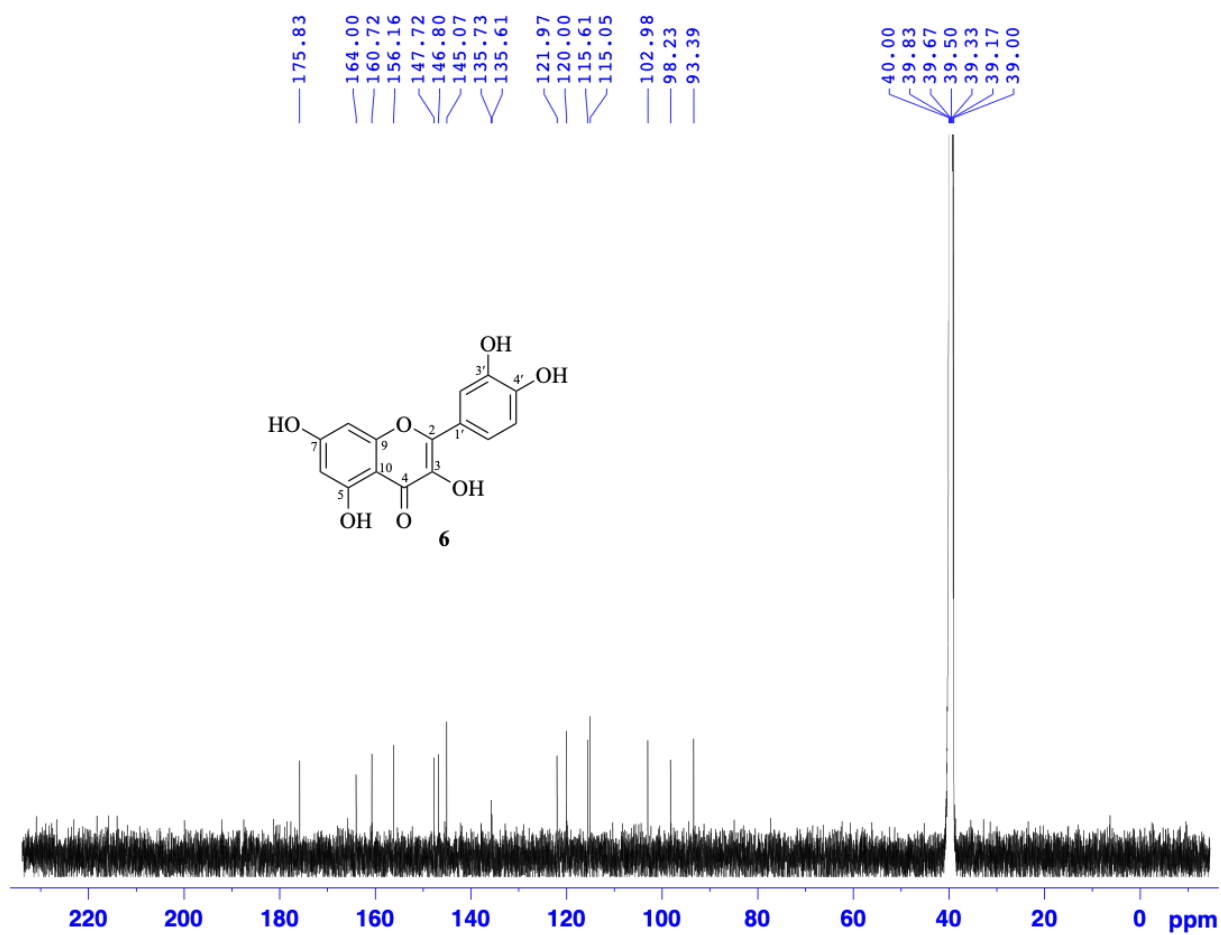


Figure S25: ^{13}C -NMR (125 MHz, $\text{DMSO-}d_6$) Spectrum of Quercetin (6)

Quercitrin (7): ESI-MS: $m/z = 301$ $[M-H-146]^-$ ($C_{21}H_{20}O_{11}$);

1H NMR (500 MHz, $DMSO-d_6$) data (Table S3); ^{13}C NMR (125 MHz, $DMSO-d_6$) data (Table S4).

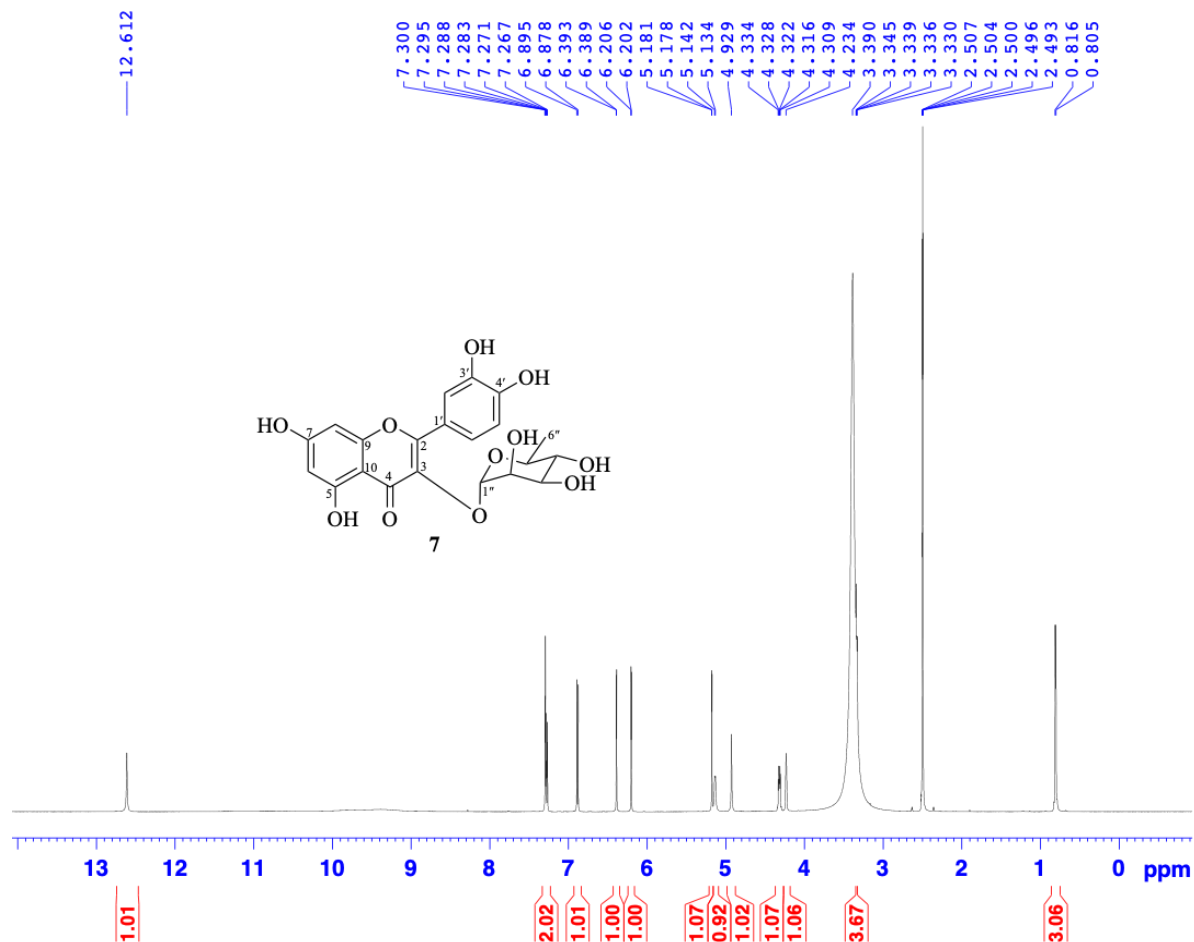


Figure S26: 1H -NMR (500 MHz, $DMSO-d_6$) Spectrum of Quercitrin (7)

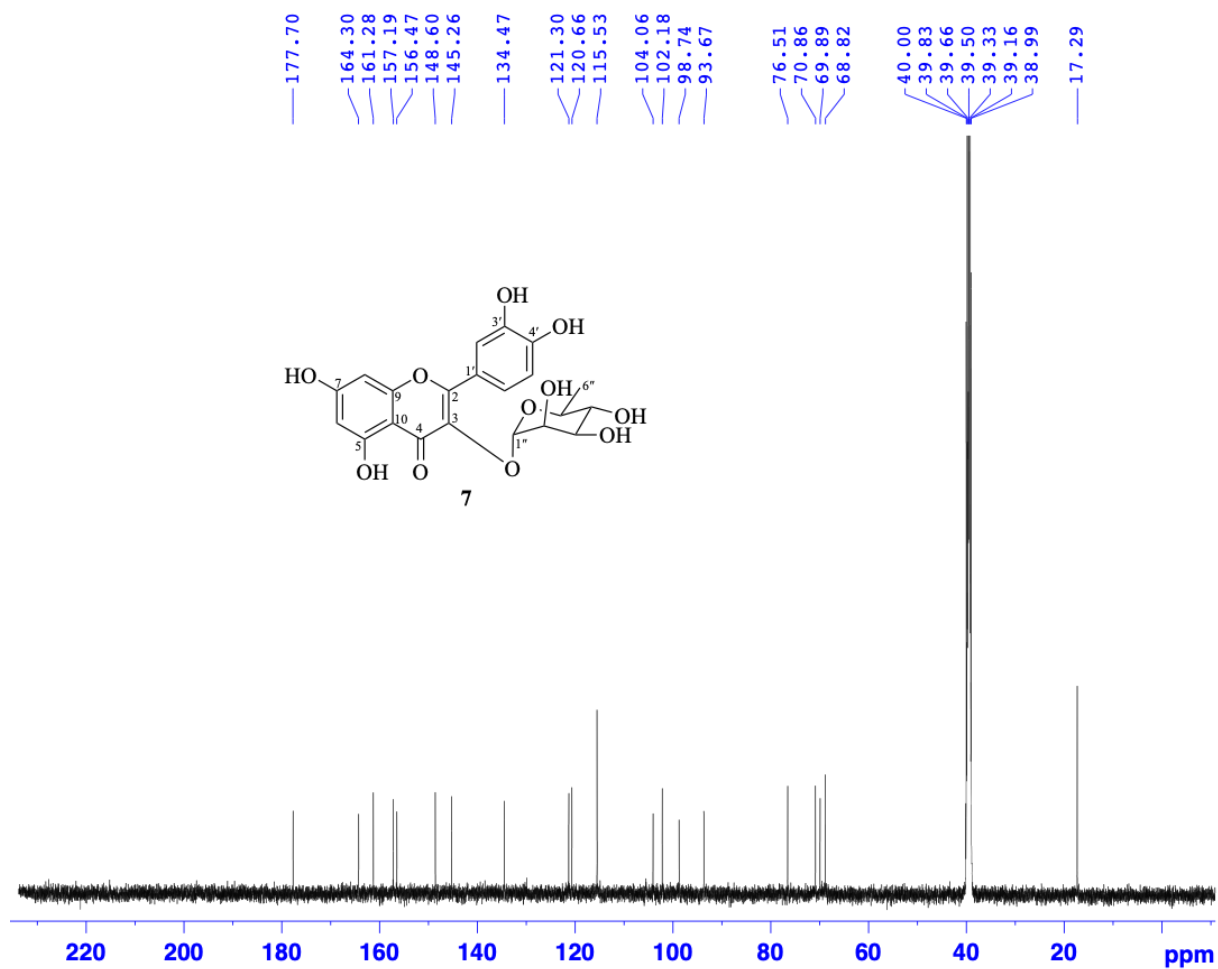


Figure S27: ^{13}C -NMR (125 MHz, $\text{DMSO-}d_6$) Spectrum of Quercitrin (7)

Isoquercitrin (8): ESI-MS (positive): m/z 465[M+H]⁺ (C₂₁H₂₁O₁₂), 303[M+H-162]⁺ (C₁₅H₁₁O₇);
¹H NMR (500 MHz, DMSO-*d*₆) data (Table S3); ¹³C NMR (125 MHz, DMSO-*d*₆) data (Table S4).

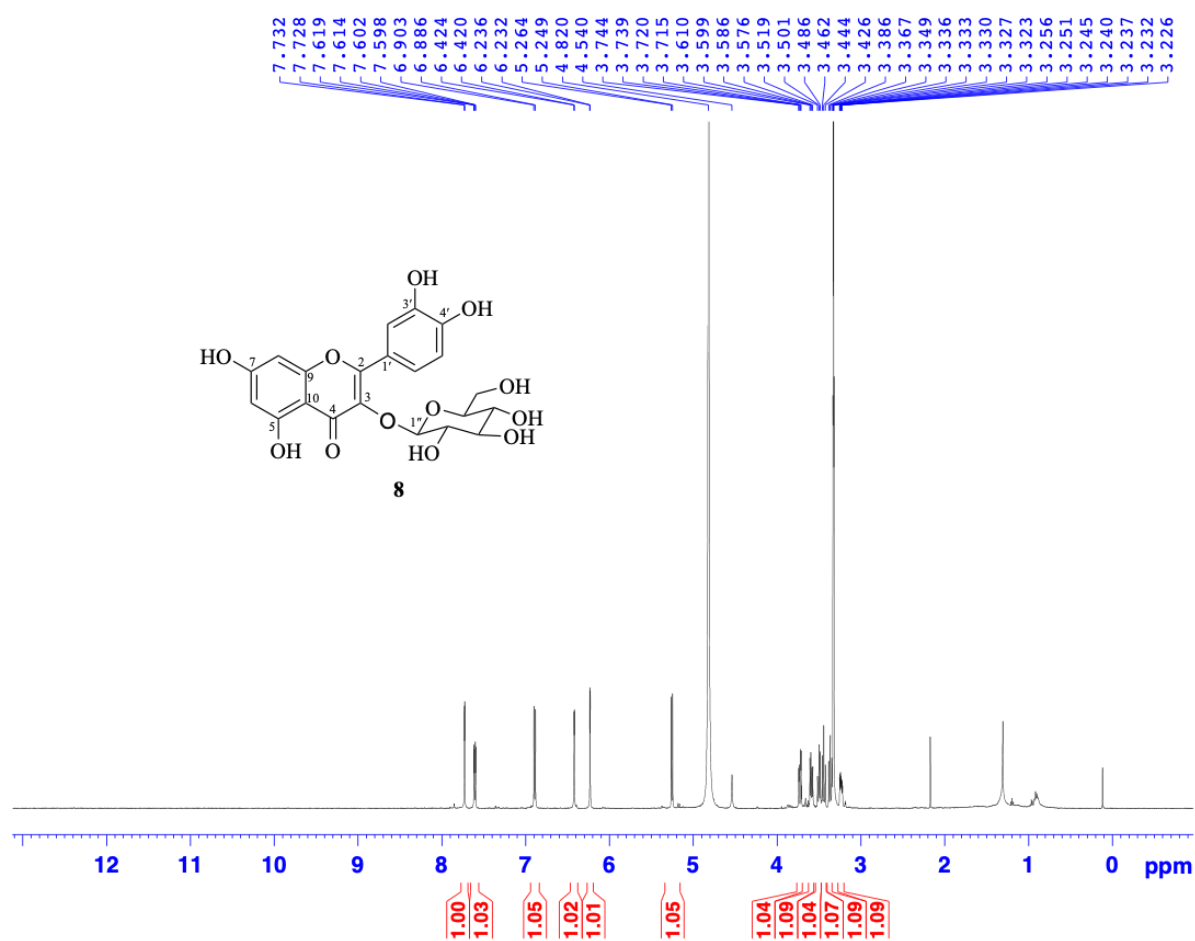


Figure S28: ¹H-NMR (500 MHz, CD₃OD) Spectrum of Isoquercitrin (8)

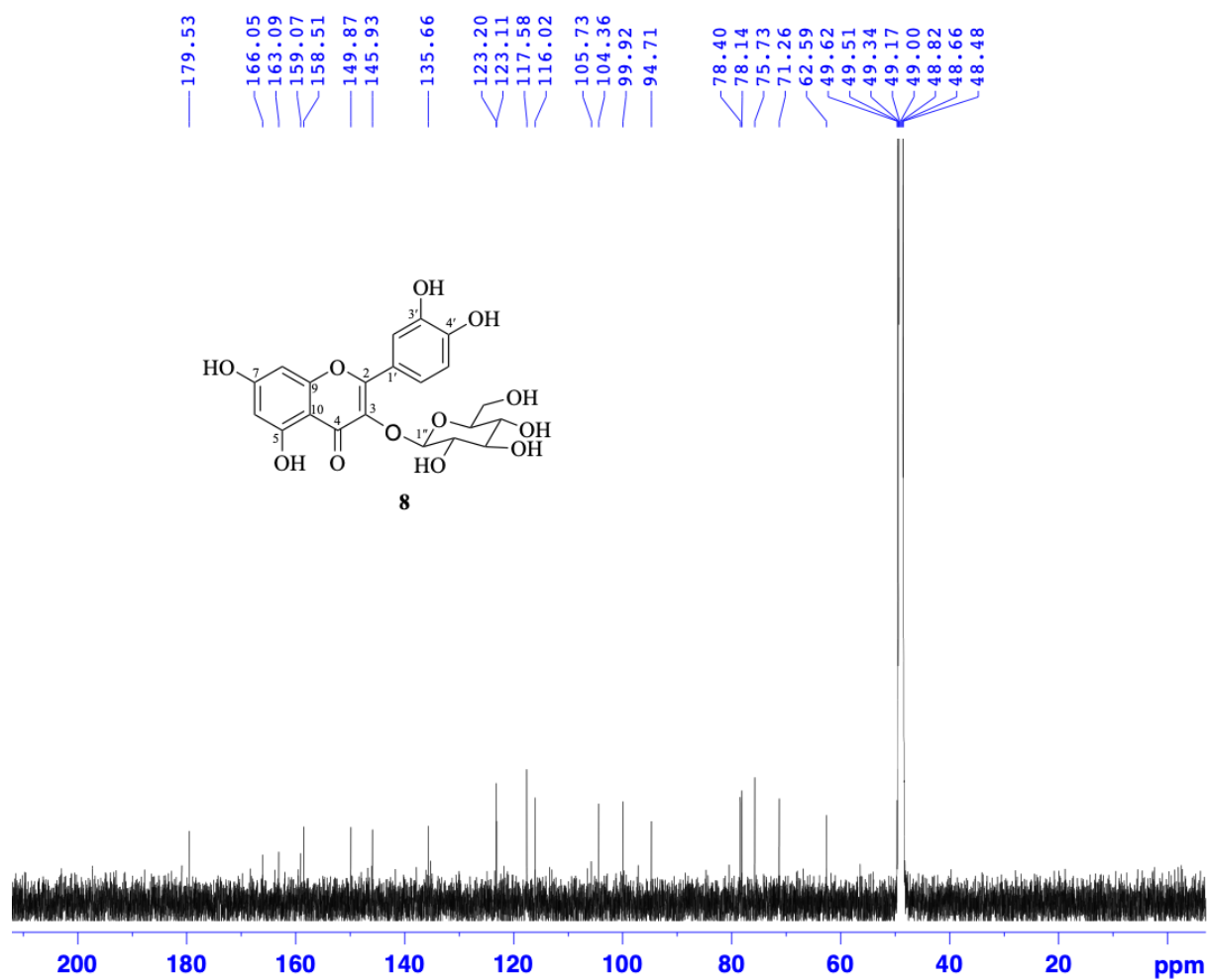


Figure S29: ^{13}C -NMR (125 MHz, CD_3OD) Spectrum of Isoquercitrin (8)

Rutin (9): ^1H NMR (500 MHz, CD_3OD) data (Table S3); ^{13}C NMR (125 MHz, CD_3OD) data (Table S4).

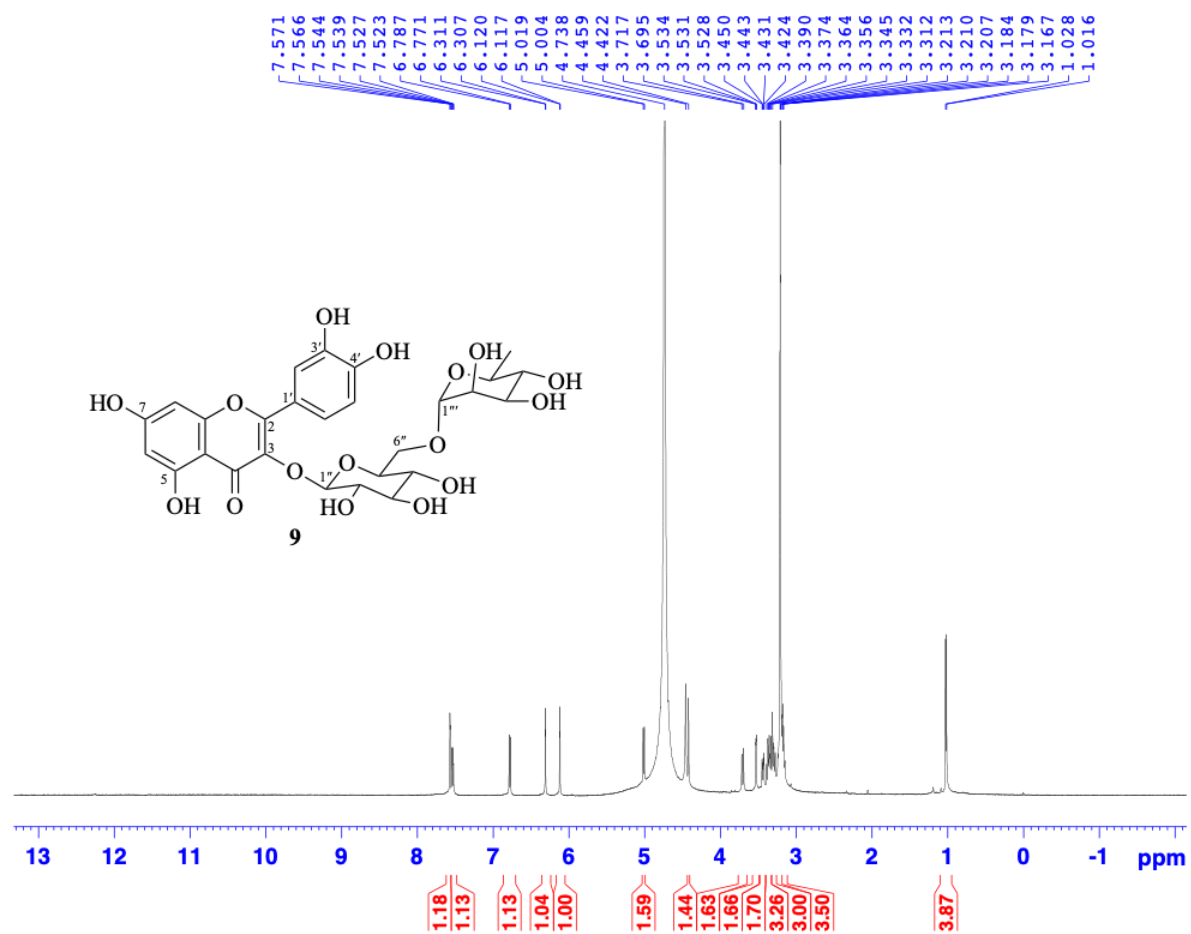


Figure S30: ^1H -NMR (500 MHz, CD_3OD) Spectrum of Rutin (9)

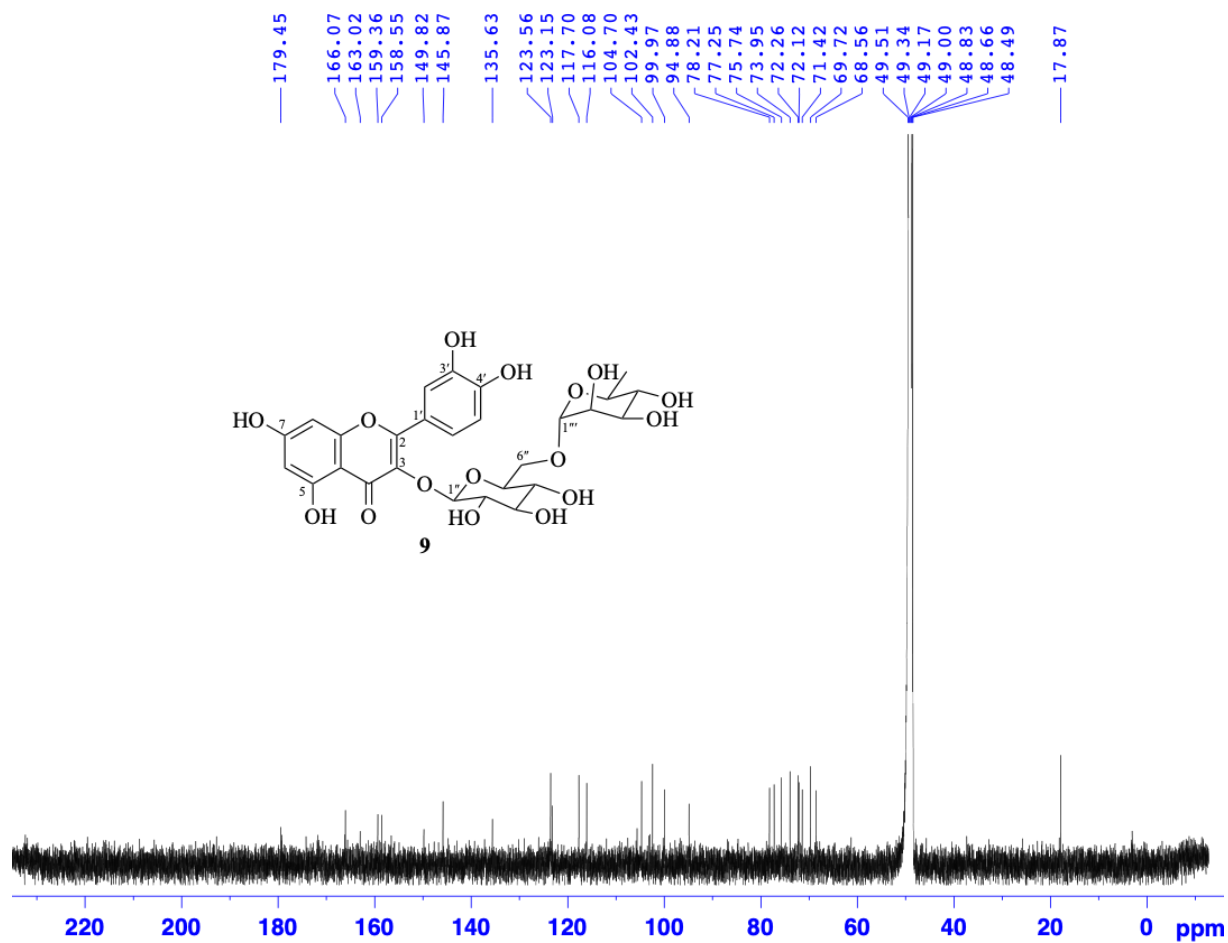


Figure S31: ^{13}C -NMR (125 MHz, CD_3OD) Spectrum of Rutin (9)

Afzelin (10): ^1H NMR (500 MHz, $\text{DMSO-}d_6$) data (Table S3); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) data (Table S4).

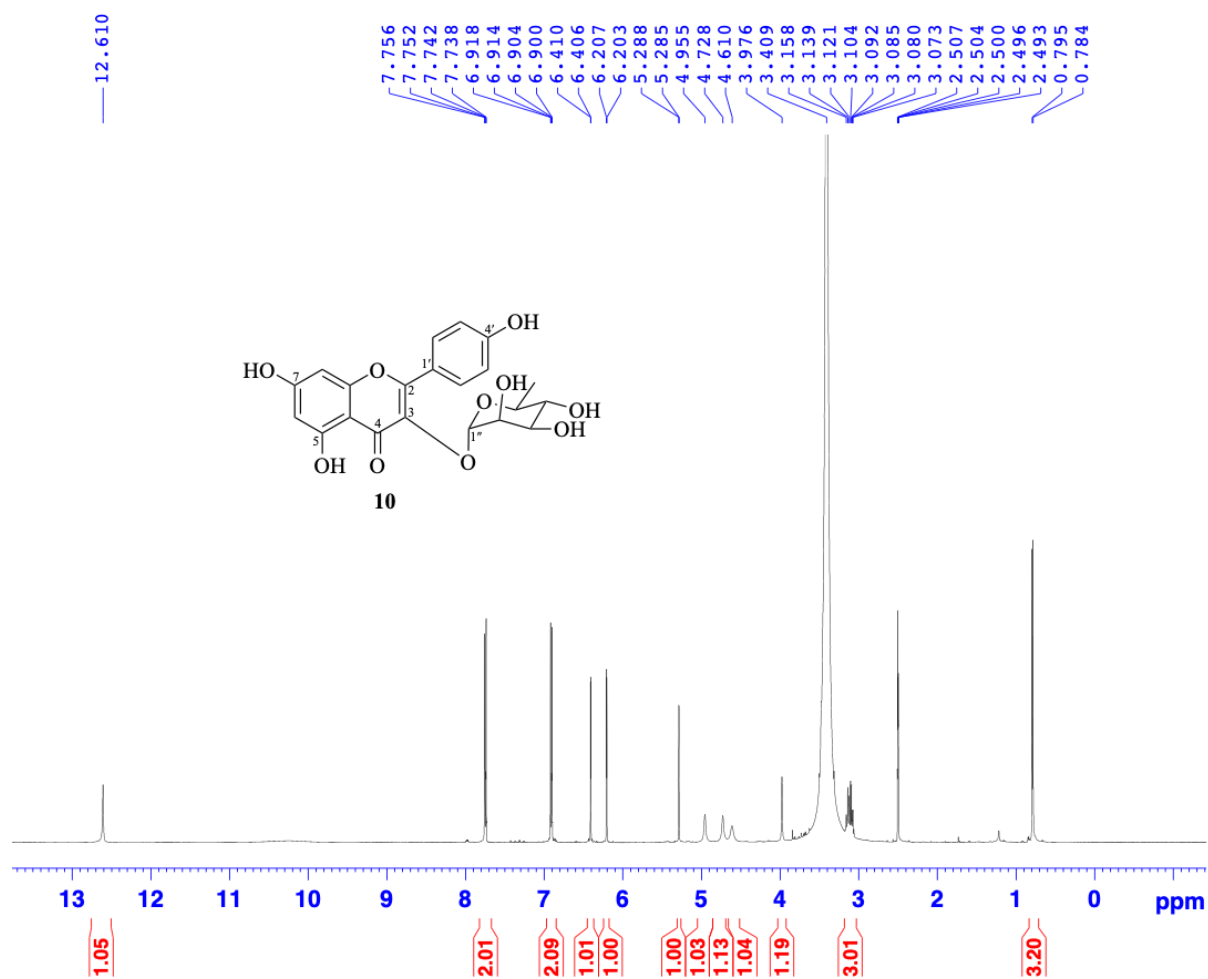


Figure S32: ^1H -NMR (500 MHz, $\text{DMSO-}d_6$) Spectrum of Afzelin (10)

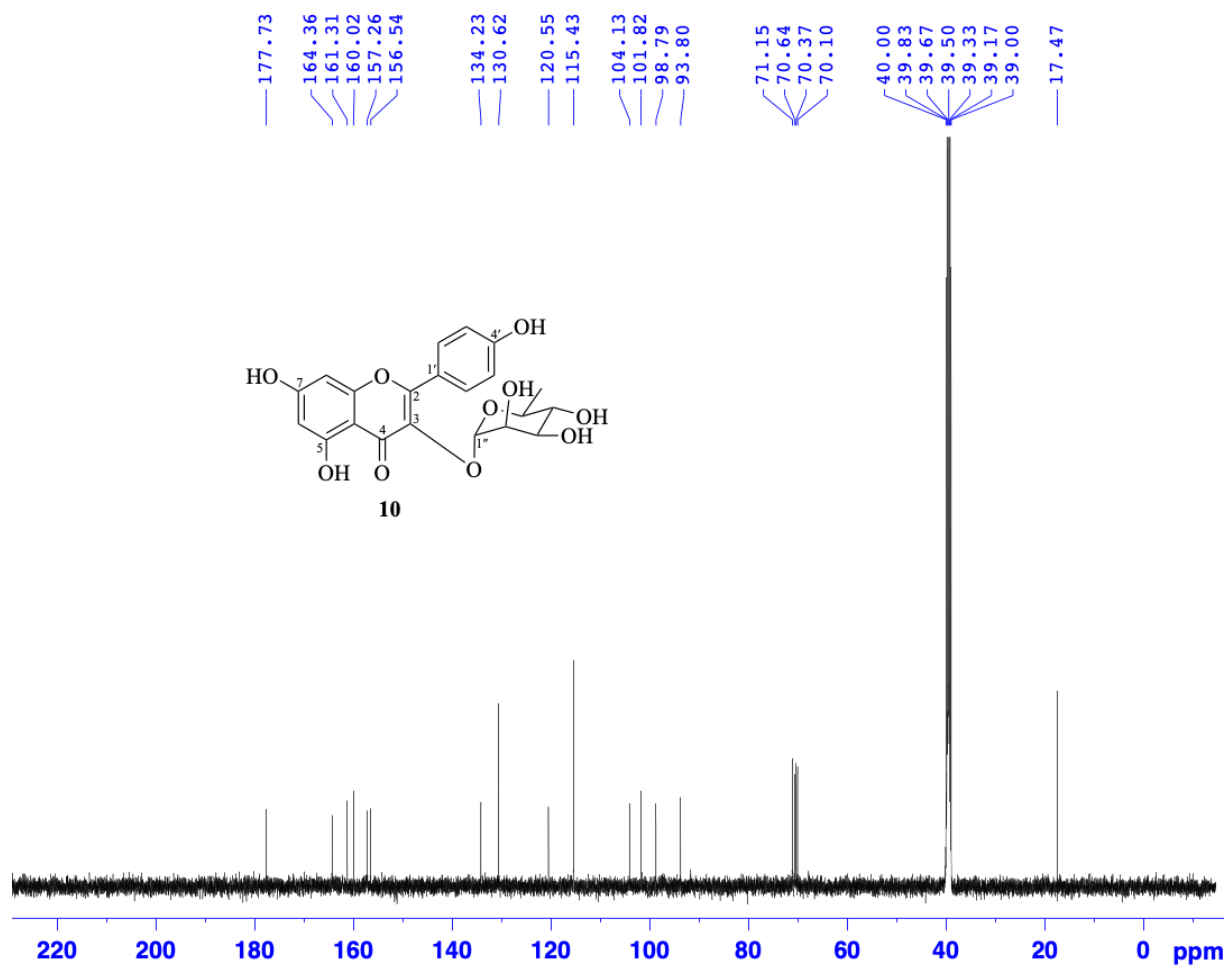


Figure S33: ¹³C-NMR (125 MHz, DMSO-*d*₆) Spectrum of Afzelin (10)

Astragalin (11): ^1H NMR (500 MHz, $\text{DMSO-}d_6$) data (Table S3); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) data (Table S4).

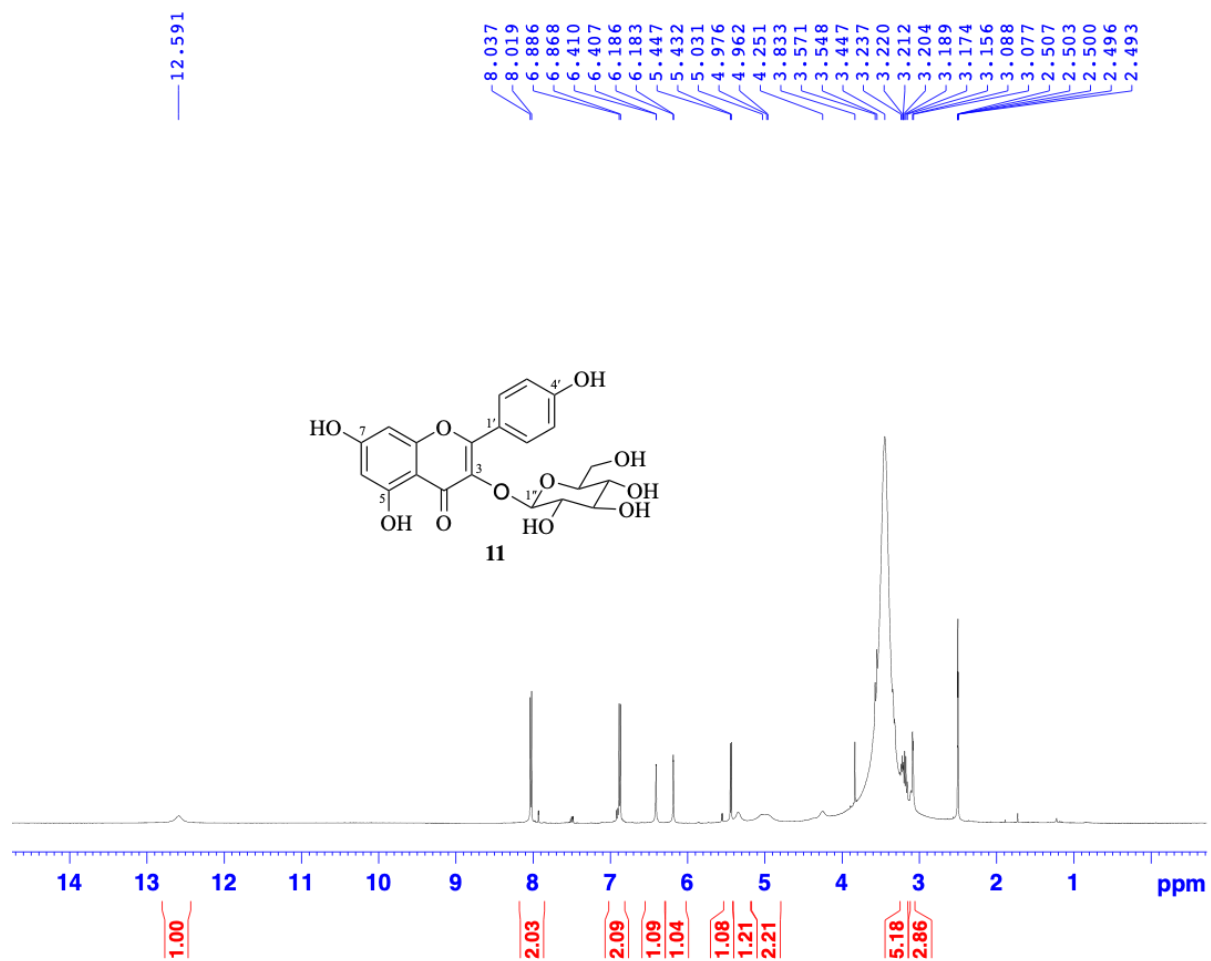


Figure S34: ^1H -NMR (500 MHz, $\text{DMSO-}d_6$) Spectrum of Astragalin (11)

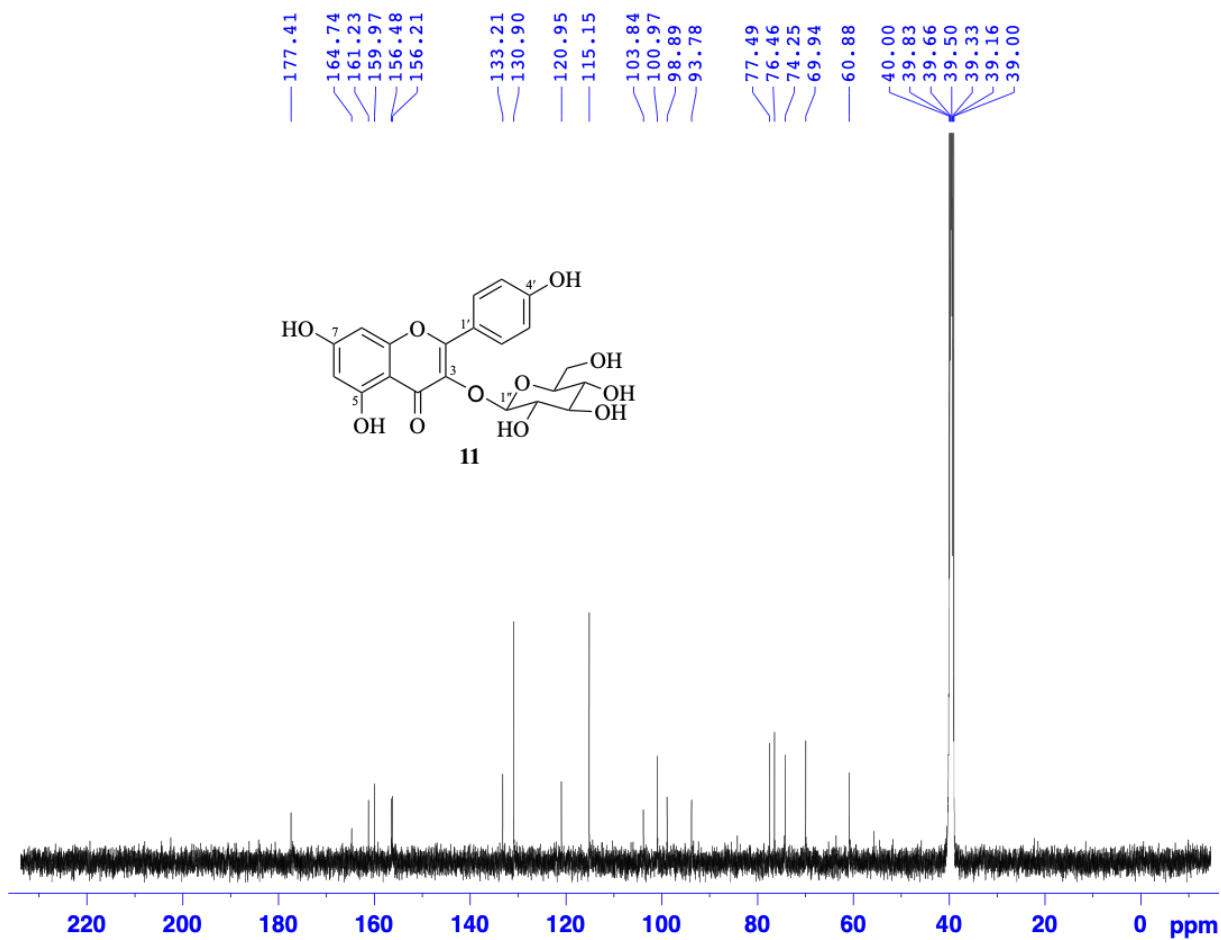


Figure S35: ^{13}C -NMR (125 MHz, $\text{DMSO-}d_6$) Spectrum of Astragalin (11)

Naringenin (12): ^1H NMR (500 MHz, CD_3OD) data (Table S3); ^{13}C NMR (125 MHz, CD_3OD) data (Table S4).

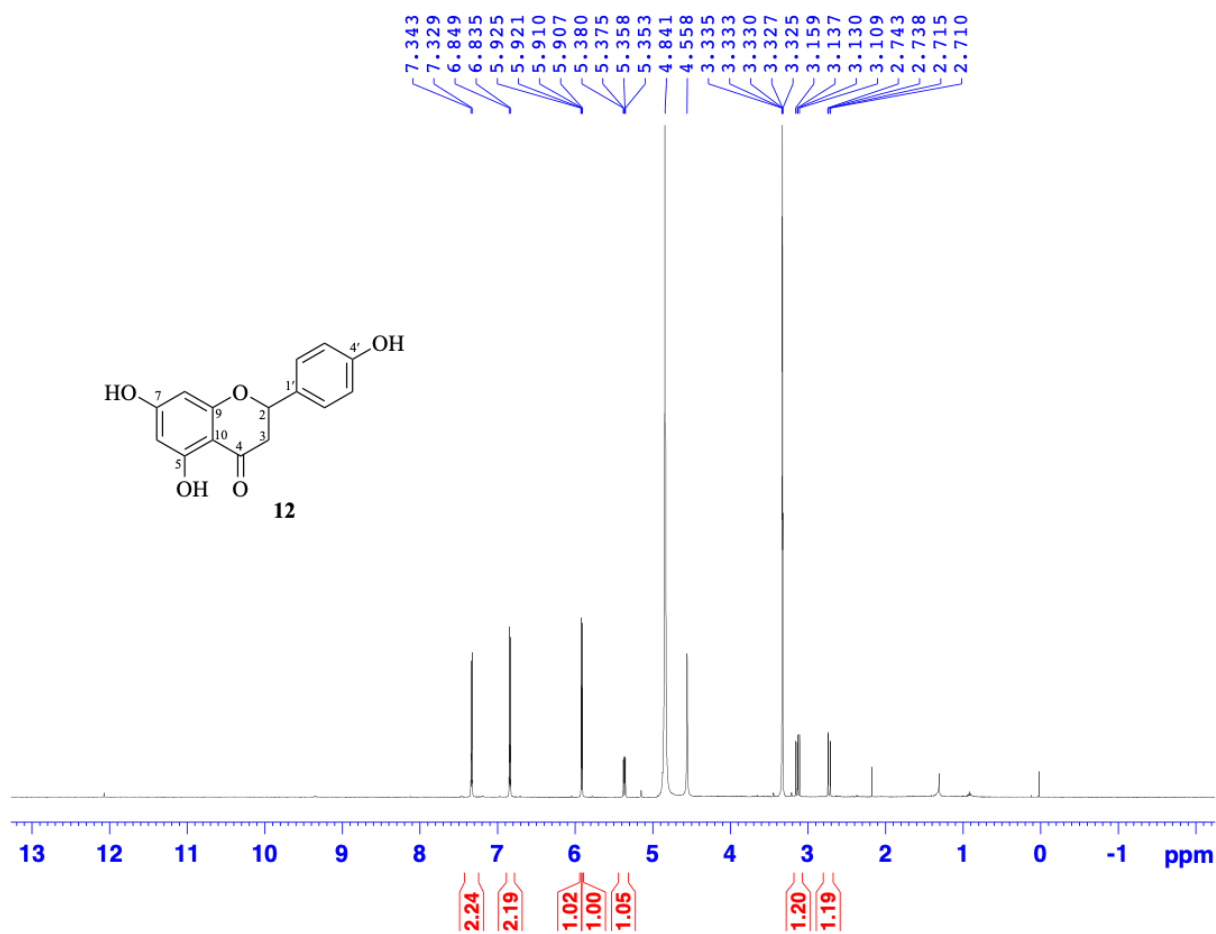


Figure S36: ^1H -NMR (500 MHz, CD_3OD) Spectrum of Naringenin (12)

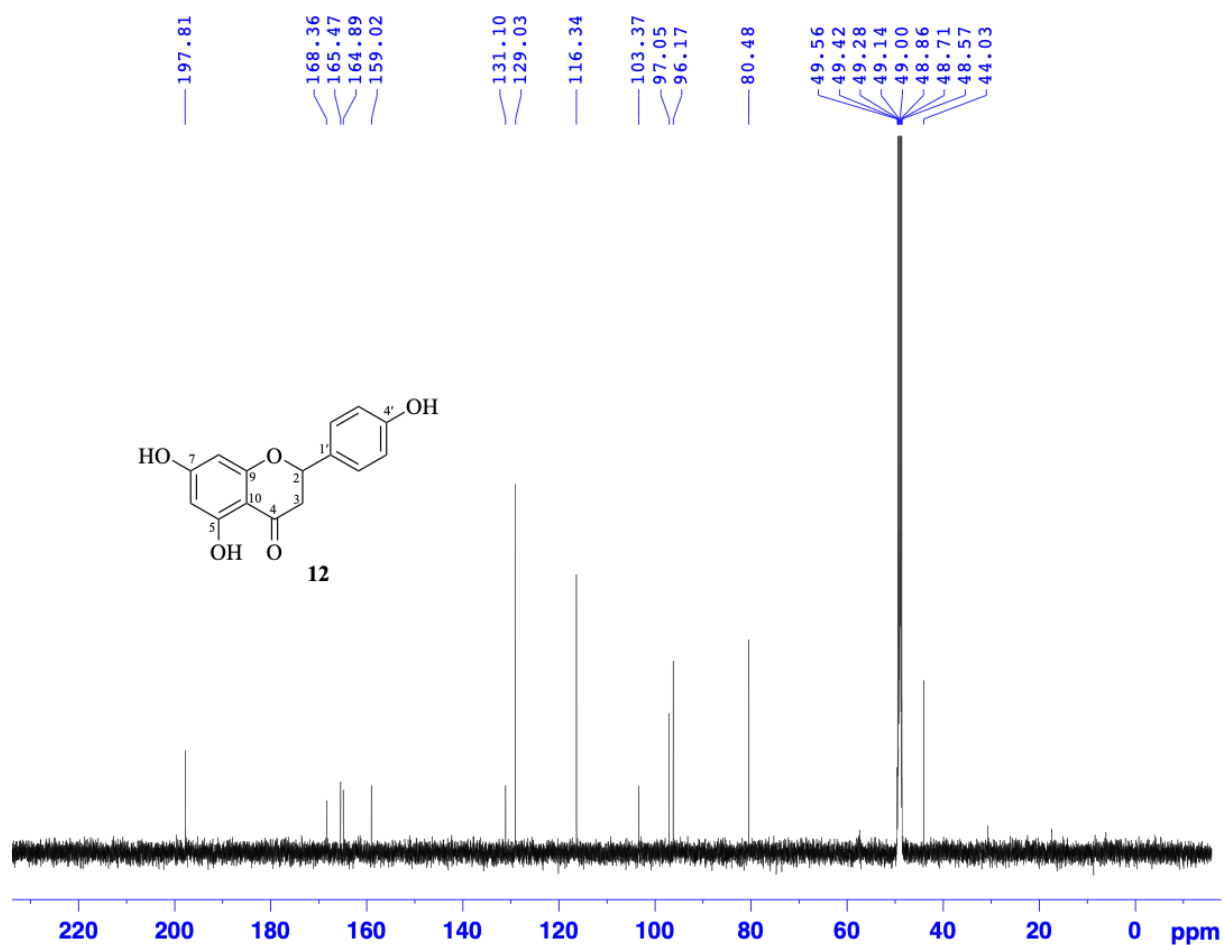


Figure S37: ¹³C-NMR (125 MHz, CD₃OD) Spectrum of Naringenin (12)

Myrciaphenone A (13): ^1H NMR (500 MHz, CD_3OD) δ : 6.21 (1H, *d*, $J = 2.5$ Hz, H-3), 5.97 (1H, *d*, $J = 2.5$ Hz, H-5), 5.05 (1H, *d*, $J = 7.5$ Hz, H-1'), 3.94 (1H, *dd*, $J = 2.0, 12.0$ Hz, H-6'a), 3.75 (1H, *dd*, $J = 5.5, 12.0$ Hz, H-6'b), 3.55 (1H, *t*, $J = 9.0$ Hz, H-2'), 3.48 (2H, *m*, H-3', H-5'), 3.44 (1H, *t*, $J = 9.0$ Hz, H-4'), 2.71 (3H, *s*, H_3 -8); ^{13}C NMR (125 MHz, CD_3OD) δ : 204.8 (C-7), 166.2 (C-6), 165.7 (C-4), 162.4 (C-2), 105.5 (C-1), 102.0 (C-1'), 98.2 (C-5), 95.4 (C-3), 78.5 (C-3'), 78.3 (C-5'), 74.7 (C-2'), 71.1 (C-4'), 62.4 (C-6'), 33.4 (C-8).

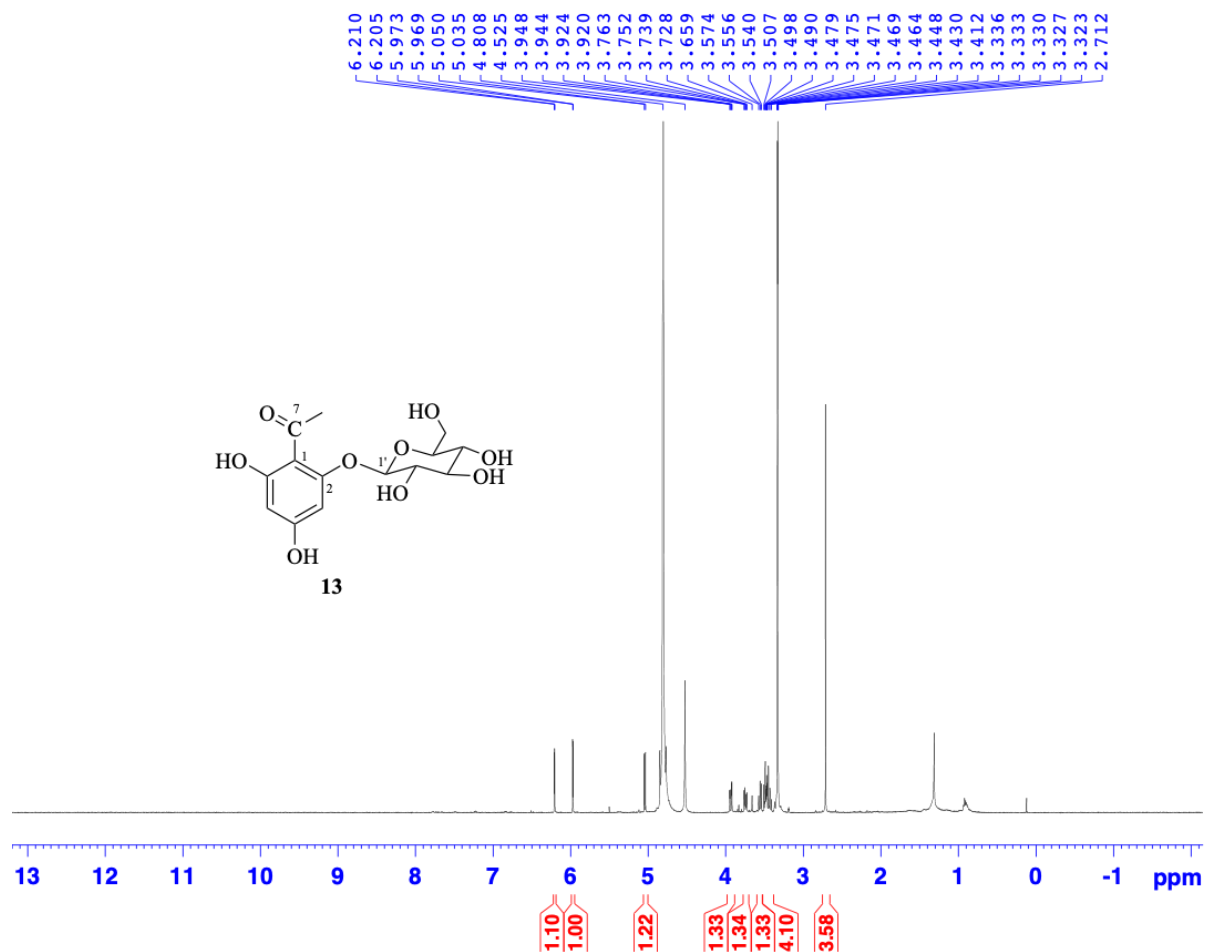


Figure S38: ^1H -NMR (500 MHz, CD_3OD) Spectrum of Myrciaphenone A (13)

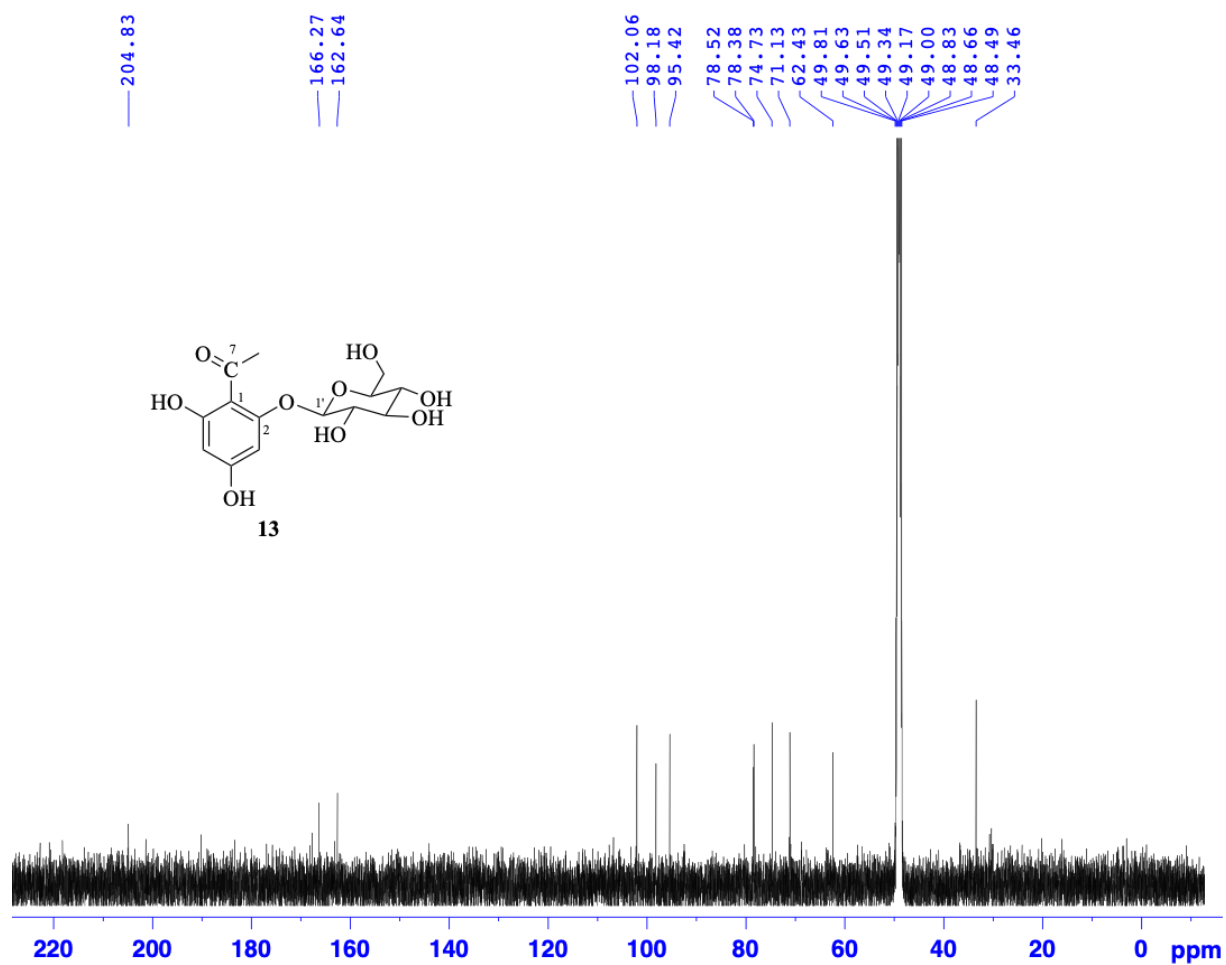


Figure S39: ¹³C-NMR (125 MHz, CD₃OD) Spectrum of Myrciaphenone A (13)

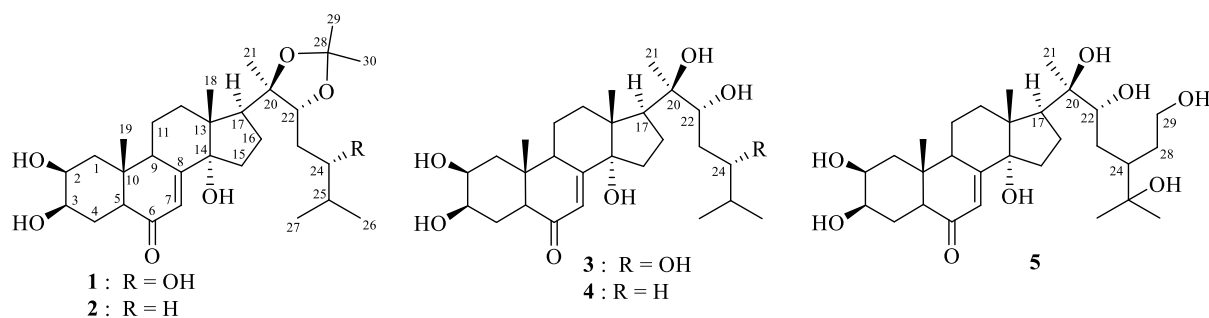


Table S1: ^1H NMR (500 MHz) data spectroscopic of compounds **1-5** (δ in ppm, J in Hz)

| Position | 1 ^a | 2 ^a | 3 ^b | 4 ^b | 5 ^c |
|----------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 1 | 1.77 <i>m</i> , 1.39 <i>m</i> | 1.77 <i>m</i> , 1.38 <i>m</i> | 1.80 <i>m</i> , 1.44 <i>m</i> | 1.83 <i>m</i> , 1.47 <i>m</i> | 1.62 <i>m</i> , 1.26 <i>m</i> |
| 2 | 3.83 <i>brd</i> (10.5) | 3.82 <i>m</i> | 3.86 <i>brd</i> (12.0) | 3.86 <i>td</i> (4.2, 7.2) | 3.77 <i>brs</i> |
| 3 | 3.92 <i>m</i> | 3.90 <i>m</i> | 3.97 <i>brs</i> | 3.97 <i>brd</i> (2.4) | 3.62 <i>m</i> |
| 4 | 1.65 <i>m</i> | 1.66 <i>m</i> | 1.72 <i>m</i> | 1.73 <i>m</i> | 1.62 <i>m</i> , 1.50 <i>m</i> |
| 5 | 2.32 <i>m</i> | 2.33 <i>m</i> | 2.41 <i>dd</i> (4.5, 12.5) | 2.41 <i>m</i> | 2.21 <i>dd</i> (4.0, 13.0) |
| 6 | - | - | - | - | - |
| 7 | 5.73 <i>d</i> (2.5) | 5.72 <i>d</i> (2.5) | 5.83 <i>brs</i> | 5.83 <i>d</i> (2.4) | 5.63 <i>d</i> (1.5) |
| 8 | - | - | - | - | - |
| 9 | 3.14 <i>m</i> | 3.16 <i>m</i> | 3.17 <i>m</i> | 3.18 <i>m</i> | 3.01 <i>m</i> |
| 10 | - | - | - | - | - |
| 11 | 1.79 <i>m</i> , 1.65 <i>m</i> | 1.76 <i>m</i> , 1.63 <i>m</i> | 1.82 <i>m</i> , 1.69 <i>m</i> | 1.82 <i>m</i> , 1.70 <i>m</i> | 1.65 <i>m</i> , 1.53 <i>m</i> |
| 12 | 2.14 <i>td</i> (6.0, 15.6) | 2.19 <i>td</i> (5.0, 12.5) | 2.14 <i>td</i> (4.5, 13.0) | 2.14 <i>td</i> (4.8, 13.2) | 1.80 <i>m</i> |
| | 1.79 <i>m</i> | 1.81 <i>m</i> | 1.88 <i>m</i> | 1.90 <i>m</i> | 1.50 <i>m</i> |
| 13 | - | - | - | - | - |
| 14 | - | - | - | - | - |
| 15 | 1.92 <i>m</i> , 1.67 <i>m</i> | 1.95 <i>m</i> , 1.67 <i>m</i> | 1.98 <i>m</i> , 1.62 <i>m</i> | 2.00 <i>m</i> , 1.60 <i>m</i> | 2.03 <i>m</i> , 1.74 <i>m</i> |
| 16 | 2.04 <i>m</i> , 1.98 <i>m</i> | 2.19 <i>m</i> , 1.87 <i>m</i> | 2.01 <i>m</i> , 1.69 <i>m</i> | 2.0 <i>m</i> , 1.73 <i>m</i> | 1.87 <i>m</i> , 1.52 <i>m</i> |
| 17 | 2.34 <i>m</i> | 2.34 <i>m</i> | 2.36 <i>m</i> | 2.39 <i>m</i> | 2.26 <i>m</i> |
| 18 | 0.81 <i>s</i> | 0.83 <i>s</i> | 0.91 <i>s</i> | 0.91 <i>s</i> | 0.77 <i>s</i> |
| 19 | 0.91 <i>s</i> | 0.93 <i>s</i> | 0.98 <i>s</i> | 0.98 <i>s</i> | 0.84 <i>s</i> |
| 20 | - | - | - | - | - |
| 21 | 1.17 <i>s</i> | 1.16 <i>s</i> | 1.23 <i>s</i> | 1.19 <i>s</i> | 1.07 <i>s</i> |
| 22 | 3.93 <i>m</i> | 3.70 <i>dd</i> (3.0, 10.0) | 3.61 <i>m</i> | 3.34 <i>m</i> | 3.13 <i>m</i> |
| 23 | 1.61 <i>m</i> | 1.44 <i>m</i> | 1.73 <i>m</i> , 1.36 <i>m</i> | 1.47 <i>m</i> , 1.25 <i>m</i> | 1.47 <i>m</i> , 1.15 <i>m</i> |
| 24 | 3.52 <i>m</i> | 1.45 <i>m</i> , 1.26 <i>m</i> | 3.61 <i>m</i> | 1.53 <i>m</i> , 1.24 <i>m</i> | 1.45 <i>m</i> |
| 25 | 1.67 <i>m</i> | 1.58 <i>m</i> | 1.70 <i>m</i> | 1.60 <i>m</i> | - |
| 26 | 0.89 <i>d</i> (7.0) | 0.91 <i>d</i> (6.5) | 0.93 <i>d</i> (7.0) | 0.93 <i>d</i> (6.6) | 1.06 <i>s</i> |
| 27 | 0.90 <i>d</i> (7.0) | 0.91 <i>d</i> (6.5) | 0.97 <i>d</i> (7.0) | 0.94 <i>d</i> (6.6) | 1.09 <i>s</i> |
| 28 | - | - | - | - | 1.26 <i>m</i> , 1.63 <i>m</i> |
| 29 | 1.31 <i>s</i> | 1.30 <i>s</i> | - | - | 3.17 <i>m</i> , 3.29 <i>m</i> |
| 30 | 1.36 <i>s</i> | 1.36 <i>s</i> | - | - | - |
| C2-OH | 4.11 <i>d</i> (5.0) | 3.59 <i>d</i> (6.5) | - | - | 4.45 <i>d</i> (6.0) |
| C3-OH | 3.91 <i>m</i> | 3.45 <i>d</i> (2.0) | - | - | 4.34 <i>d</i> (3.0) |
| C14-OH | 4.32 <i>s</i> | 3.81 <i>s</i> | - | - | 4.67 <i>s</i> |
| C20-OH | - | - | - | - | 3.58 <i>s</i> |
| C22-OH | - | - | - | - | 4.38 <i>d</i> (5.0) |
| C24-OH | 3.68 <i>d</i> (3.5) | - | - | - | - |
| C25-OH | - | - | - | - | 4.13 <i>s</i> |

^a Recorded in CD_3COCD_3 , ^b in CD_3OD , ^c in $\text{DMSO}-d_6$

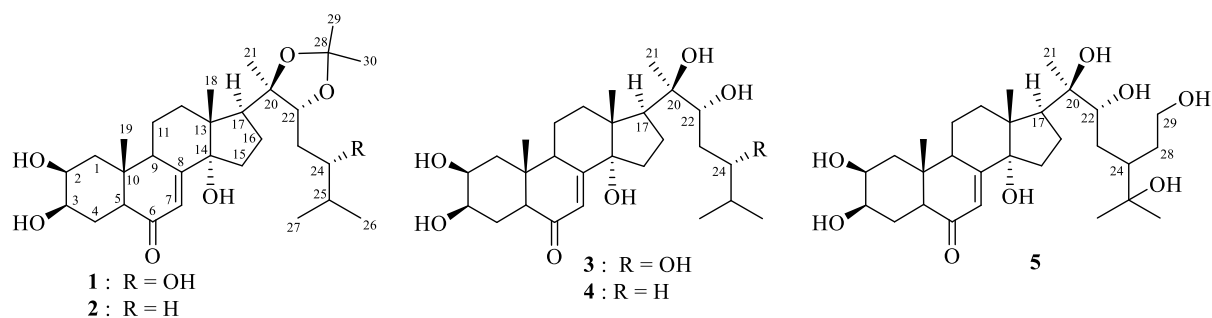


Table S2 : ^{13}C NMR (125 MHz) data spectroscopic of compounds **1-5**

| Position | 1 ^a | 2 ^a | 3 ^b | 4 ^b | 5 ^c |
|----------|----------------|-------------------|-------------------|-------------------|----------------|
| 1 | 37.4 | 37.8 | 37.4 | 37.4 | 36.6 |
| 2 | 68.1 | 68.2 | 68.7 | 68.7 | 66.8 |
| 3 | 68.0 | 68.1 | 68.5 | 68.5 | 66.6 |
| 4 | 32.0 | 32.1 | 32.8 | 32.9 | 31.6 |
| 5 | 51.1 | 51.3 | 51.8 | 51.8 | 50.1 |
| 6 | 203.9 | 202.9 | 206.4 | 206.5 | 202.8 |
| 7 | 121.8 | 122.0 | 122.2 | 122.1 | 120.5 |
| 8 | 165.2 | 164.5 | 167.9 | 168.0 | 165.3 |
| 9 | 34.4 | 34.6 | 35.1 | 35.1 | 33.2 |
| 10 | 38.6 | 38.7 | 39.3 | 39.3 | 37.7 |
| 11 | 21.0 | 21.2 | 21.5 | 21.5 | 20.1 |
| 12 | 31.8 | 32.0 | 32.5 | 32.5 | 30.3 |
| 13 | 48.0 | 48.1 | *overlap | *overlap | 46.9 |
| 14 | 84.7 | 84.8 | 85.2 | 85.2 | 83.0 |
| 15 | 31.4 | 31.7 | 31.8 | 31.8 | 30.9 |
| 16 | 22.0 | 22.1 | 21.5 | 21.5 | 20.3 |
| 17 | 49.9 | 50.1 | 50.4 | 50.5 | 48.7 |
| 18 | 17.5 | 17.5 | 18.0 | 18.0 | 17.2 |
| 19 | 24.3 | 24.4 | 24.4 | 24.4 | 23.8 |
| 20 | 85.5 | 85.2 | 77.8 | 77.9 | 76.3 |
| 21 | 22.4 | 22.4 | 21.0 | 21.0 | 21.0 |
| 22 | 80.4 | 82.3 | 77.6 ^d | 78.0 | 75.8 |
| 23 | 33.8 | 27.5 | 35.7 | 37.7 | 26.1 |
| 24 | 75.1 | 37.3 | 77.5 ^d | 30.5 | 35.6 |
| 25 | 33.7 | 28.8 | 34.1 | 29.2 | 68.8 |
| 26 | 17.4 | 22.9 ^d | 17.0 | 22.8 ^d | 29.0 |
| 27 | 19.3 | 22.8 ^d | 19.3 | 23.4 ^d | 30.0 |
| 28 | 107.6 | 107.2 | | | 41.4 |
| 29 | 27.1 | 27.2 | | | 66.6 |
| 30 | 29.2 | 29.3 | | | |

^a Recorded in CD_3COCD_3 , ^b in CD_3OD , ^c in $\text{DMSO}-d_6$

^d Assignments may be interchanged in each column

*Overlapped with intensive solvent multiplet (CD_3OD : δ_{C} 49.0)

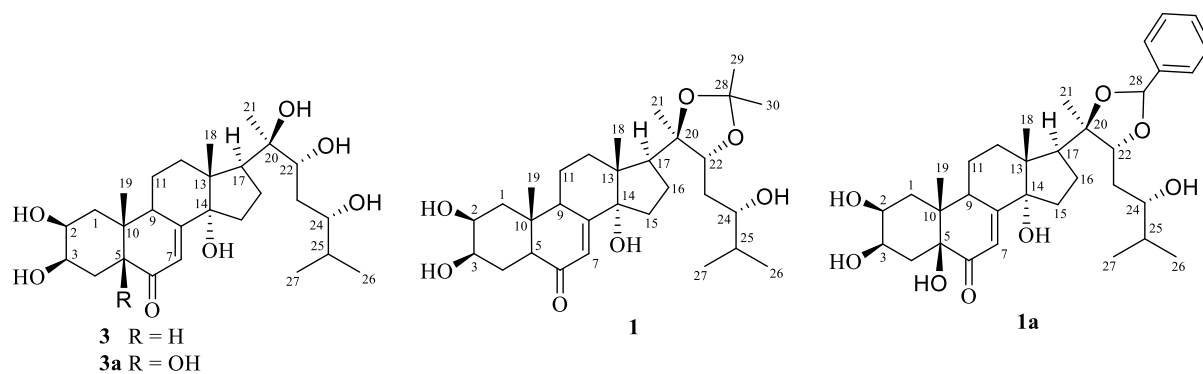


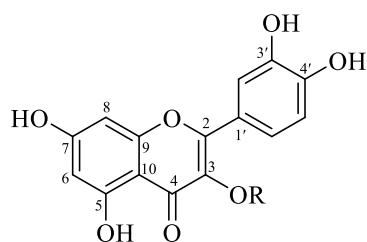
Table S3 : ^{13}C NMR data spectroscopic of compounds **1**, **3** and **1a**

| Position | 3^b | 1^a | 3a^c | 1a^c |
|----------|----------------------|----------------------|-----------------------|------------------------------------|
| 1 | 37.4 | 37.4 | 34.6 | 34.8 |
| 2 | 68.7 | 68.1 | 67.8 | 67.9 |
| 3 | 68.5 | 68.0 | 69.7 | 69.7 |
| 4 | 32.8 | 32.0 | 35.9 | 35.9 |
| 5 | 51.8 | 51.1 | 79.7 | 79.8 |
| 6 | 206.4 | 203.9 | 200.8 | 200.5 |
| 7 | 122.2 | 121.8 | 119.8 | 119.9 |
| 8 | 167.9 | 165.2 | 166.8 | 166.2 |
| 9 | 35.1 | 34.4 | 38.2 | 38.2 |
| 10 | 39.3 | 38.6 | 44.6 | 44.6 |
| 11 | 21.5 | 21.0 | 21.3 | 21.9 |
| 12 | 32.5 | 31.8 | 31.5 | 31.6 |
| 13 | *overlap | 48.0 | 48.0 | 47.8 |
| 14 | 85.2 | 84.7 | 83.9 | 83.9 |
| 15 | 31.8 | 31.4 | 32.0 | 31.6 |
| 16 | 21.5 | 22.0 | 22.0 | 22.4 |
| 17 | 50.4 | 49.9 | 49.8 | 50.7 |
| 18 | 18.0 | 17.5 | 17.8 | 17.4 |
| 19 | 24.4 | 24.3 | 17.7 | 17.1 |
| 20 | 77.8 | 85.5 | 76.8 | 85.3 |
| 21 | 21.0 | 22.4 | 21.5 | 23.3 |
| 22 | 77.6 ^d | 80.4 | 76.7 ^d | 82.6 |
| 23 | 35.7 | 33.8 | 35.6 | 33.5 |
| 24 | 77.5 ^d | 75.1 | 77.5 ^d | 74.3 |
| 25 | 34.1 | 33.7 | 34.0 | 34.2 |
| 26 | 17.0 | 17.4 | 17.0 | 17.2 |
| 27 | 19.3 | 19.3 | 19.5 | 19.6 |
| C-acetal | - | 107.6 | - | 104.0 |
| | | Dimethyl: 27.1, 29.2 | | Phenyl: 139.9, 129.3, 128.6, 127.4 |

^a Recorded in acetone-*d*₆, ^b in CD₃OD, ^c in pyridine-*d*₅

^d Assignments may be interchanged in each column

3a: ponasterone C; **1a**: ponasterone C-20,22-benzylidene acetal [11]

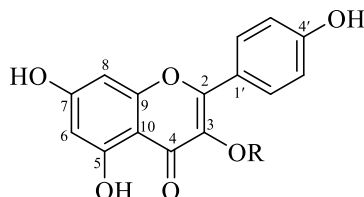


6 : R = H

7 : R = O- α -L-Rha

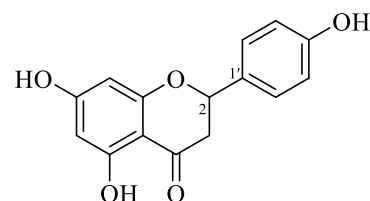
8 : R = O- β -D-Glc

9 : R = O- β -D-Glc⁶- α -L-Rha



10 : R = O- α -L-Rha

11 : R = O- β -D-Glc

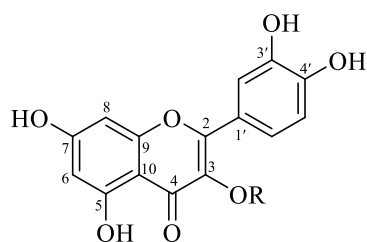


12

Table S4 : ¹H NMR (500 MHz) data spectroscopic of compounds **6-12** (δ in ppm, *J* in Hz)

| Position | 6 ^a | 7 ^a | 8 ^b | 9 ^b | 10 ^a | 11 ^a | 12 ^b |
|-----------|---------------------------|---------------------------|--|------------------------------|------------------------|------------------------|---|
| 2 | - | - | - | - | - | - | 5.37 <i>dd</i> (13.3) |
| 3 | - | - | - | - | - | - | 3.13 <i>dd</i> (13.0, 17.0) 2.71 <i>dd</i> (3.0, 17.0) |
| 4 | - | - | - | - | - | - | - |
| 5 | - | - | - | - | - | - | - |
| 6 | 6.17 <i>d</i> (1.5) | 6.20 <i>d</i> (2.0) | 6.23 <i>d</i> (2.0) | 6.12 <i>d</i> (2.0) | 6.20 <i>d</i> (2.0) | 6.18 <i>d</i> (1.5) | 5.92 <i>d</i> (2.0) |
| 7 | - | - | - | - | - | - | - |
| 8 | 6.39 <i>d</i> (1.5) | 6.39 <i>d</i> (2.0) | 6.42 <i>d</i> (2.0) | 6.31 <i>d</i> (2.0) | 6.41 <i>d</i> (2.0) | 6.41 <i>d</i> (1.5) | 5.91 <i>d</i> (2.0) |
| 9 | - | - | - | - | - | - | - |
| 10 | - | - | - | - | - | - | - |
| 1' | - | - | - | - | - | - | - |
| 2' | 7.66 <i>d</i> (1.0) | 7.30 <i>d</i> (2.5) | 7.73 <i>d</i> (2.0) | 7.57 <i>d</i> (2.5) | 7.75 <i>d</i> (9.0) | 8.03 <i>d</i> (9.0) | 7.34 <i>d</i> (8.4) |
| 3' | - | - | - | - | 6.91 <i>d</i> (9.0) | 6.88 <i>d</i> (9.0) | 6.84 <i>d</i> (8.4) |
| 4' | - | - | - | - | - | - | - |
| 5' | 6.88 <i>d</i> (8.5) | 6.89 <i>d</i> (8.5) | 6.90 <i>d</i> (8.5) | 6.78 <i>d</i> (8.5) | 6.91 <i>d</i> (9.0) | 6.88 <i>d</i> (9.0) | 6.84 <i>d</i> (8.4) |
| 6' | 7.53 <i>dd</i> (1.0, 8.5) | 7.28 <i>dd</i> (2.5, 8.5) | 7.61 <i>dd</i> (2.0, 8.5) | 7.53 <i>dd</i> (2.5, 8.5) | 7.75 <i>d</i> (9.0) | 8.03 <i>d</i> (9.0) | 7.34 <i>d</i> (8.4) |
| 5-OH | 12.46 <i>s</i> | 12.61 <i>s</i> | - | - | 12.61 <i>s</i> | 12.59 <i>brs</i> | - |
| 1'' | - | 5.18 <i>d</i> (1.5) | 5.26 <i>d</i> (7.5) | 5.01 <i>d</i> (7.5) | 5.28 <i>d</i> (1.5) | 5.44 <i>d</i> (7.5) | - |
| 2'' | - | 3.33 <i>m</i> | 3.50 <i>t</i> (9.0) | 3.16-3.39 | 3.10 | 3.08-3.54 | - |
| 3'' | - | 4.23 <i>m</i> | 3.44 <i>t</i> (9.0) | (6H, <i>m</i>) | (3H, <i>m</i>) | (6H, <i>m</i>) | - |
| 4'' | - | 4.32 <i>m</i> | 3.36 <i>t</i> (9.0) | - | - | - | - |
| 5'' | - | 3.33 <i>m</i> | 3.23 <i>m</i> | - | 3.97 <i>brs</i> | - | - |
| 6'' | - | 0.81 <i>d</i> (5.5) | 3.73 <i>dd</i> (2.5, 12.0) 3.59 <i>dd</i> (5.5, 12.0) | - | 0.79 <i>d</i> (5.5) | - | - |
| 1''' | - | - | - | 4.45 <i>brs</i> | - | - | - |
| 2'''-5''' | - | - | - | 3.16-3.39 (4H, <i>m</i>) | - | - | - |
| 6''' | - | - | - | 1.02 <i>d</i> (6.0) | - | - | - |

^a Recorded in DMSO-*d*₆, ^b in CD₃OD

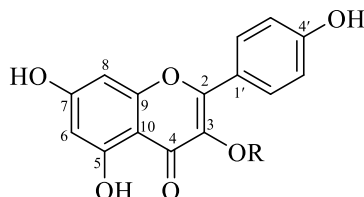


6 : R = H

7 : R = O- α -L-Rha

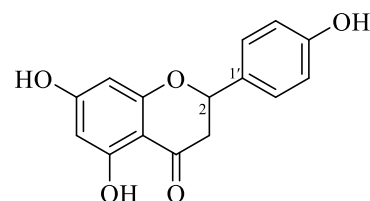
8 : R = O- β -D-Glc

9 : R = O- β -D-Glc⁶- α -L-Rha



10 : R = O- α -L-Rha

11 : R = O- β -D-Glc



12

Table S5 : ¹³C NMR (125 MHz) data spectroscopic of compounds **6-12**

| Position | 6 ^a | 7 ^a | 8 ^b | 9 ^b | 10 ^a | 11 ^a | 12 ^b |
|----------|-----------------------|-----------------------|-----------------------|-----------------------|------------------------|------------------------|------------------------|
| 2 | 146.8 | 156.5 | 158.5 | 158.6 | 157.3 | 156.2 | 80.5 |
| 3 | 135.6 | 134.5 | 135.7 | 135.6 | 134.2 | 133.2 | 44.0 |
| 4 | 175.8 | 177.7 | 179.5 | 179.5 | 177.7 | 177.4 | 197.8 |
| 5 | 160.7 | 161.3 | 163.1 | 163.0 | 161.3 | 161.2 | 165.5 |
| 6 | 98.2 | 98.7 | 99.9 | 100.0 | 98.8 | 98.9 | 97.1 |
| 7 | 164.0 | 164.3 | 166.1 | 166.1 | 164.4 | 164.7 | 168.4 |
| 8 | 93.4 | 93.7 | 94.7 | 94.9 | 93.8 | 93.8 | 96.2 |
| 9 | 156.2 | 157.2 | 159.1 | 159.4 | 156.6 | 156.5 | 164.9 |
| 10 | 103.0 | 104.1 | 105.7 | 105.5 | 104.1 | 103.8 | 103.4 |
| 1' | 122.0 | 120.7 | 123.1 | 123.2 | 120.6 | 121.0 | 131.1 |
| 2' | 115.1 | 115.5 | 117.6 | 117.7 | 130.6 | 130.9 | 129.0 |
| 3' | 145.1 | 145.3 | 145.9 | 145.9 | 115.4 | 115.2 | 116.3 |
| 4' | 147.7 | 148.6 | 149.9 | 149.8 | 160.0 | 160.0 | 159.0 |
| 5' | 115.6 | 115.5 | 116.0 | 116.1 | 115.4 | 115.2 | 116.3 |
| 6' | 120.0 | 121.3 | 123.2 | 123.6 | 130.6 | 130.9 | 129.0 |
| 1'' | | 102.2 | 104.4 | 104.7 | 101.9 | 101.0 | |
| 2'' | | 70.9 | 75.7 | 75.7 | 70.4 | 74.3 | |
| 3'' | | 68.8 | 78.1 | 77.3 | 70.6 | 76.5 | |
| 4'' | | 76.5 | 71.3 | 71.4 | 71.2 | 69.9 | |
| 5'' | | 69.9 | 78.4 | 78.2 | 70.1 | 77.5 | |
| 6'' | | 17.3 | 62.6 | 68.4 | 17.5 | 60.9 | |
| 1''' | | | | 102.4 | | | |
| 2''' | | | | 72.3 | | | |
| 3''' | | | | 72.1 | | | |
| 4''' | | | | 74.0 | | | |
| 5''' | | | | 69.7 | | | |
| 6''' | | | | 17.9 | | | |

^a Recorded in DMSO-*d*₆, ^b in CD₃OD