## Supporting Information

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# Phytochemical Investigation of Endemic *Sideritis cypria* Post

**Duygu Yiğit Hanoğlu[1]*, Azmi Hanoğlu[2], Hasan Yusufoğlu[3], Betül Demirci[4], Kemal Hüsnü Can Başer[2], İhsan Çaliş[2] and Dudu Özkum Yavuz[1]**

[1]*Department of Pharmaceutical Botany, Faculty of Pharmacy, Near East University, Lefkoşa (Nicosia), Turkish Republic of Northern Cyprus*

[2]*Department of Pharmacognosy, Faculty of Pharmacy, Near East University, Lefkoşa (Nicosia), (Nicosia), Turkish Republic of Northern Cyprus*

[3]*Prince Sattam Bin Abdulaziz University, College of Pharmacy, Department of Pharmacognosy Alkharj- 11942, P.O.Box 173, Saudi Arabia*

[4]*Department of Pharmacognosy, Faculty of Pharmacy, Anadolu University, Eskişehir, Türkiye*

| Table of Contents | Page |
|---|---|

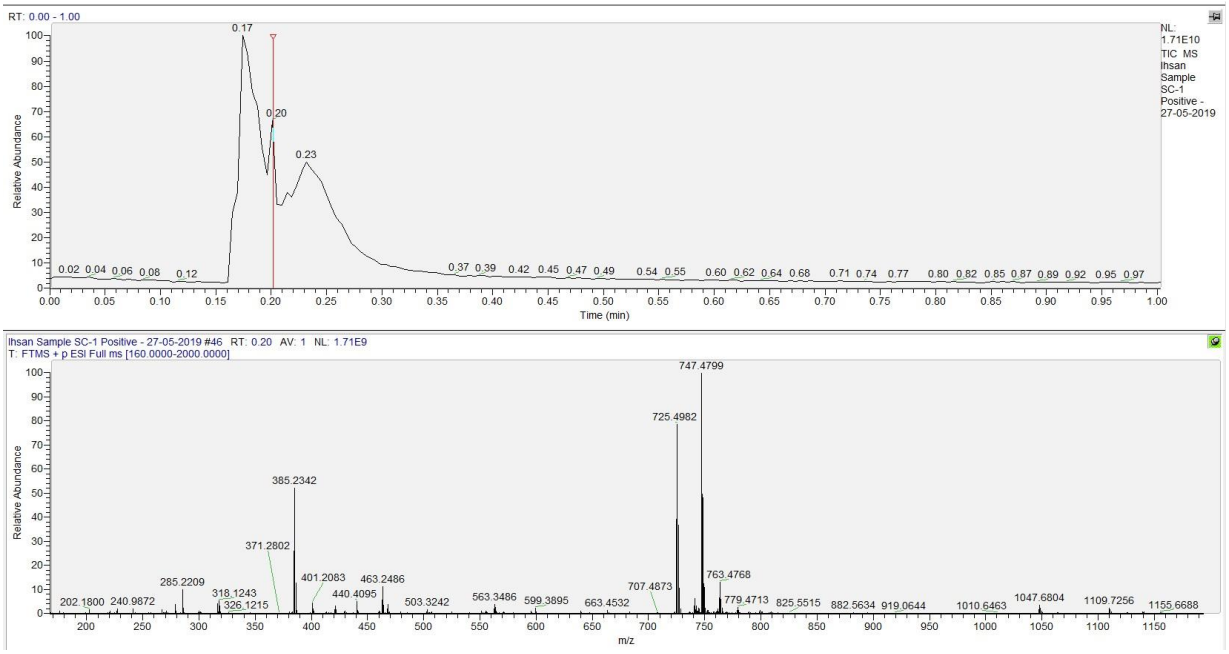


**Figure S1:** Positive- ion HR-LCMS-MS Spectrum of Compound **1&2** (Sidol & Isosidol)

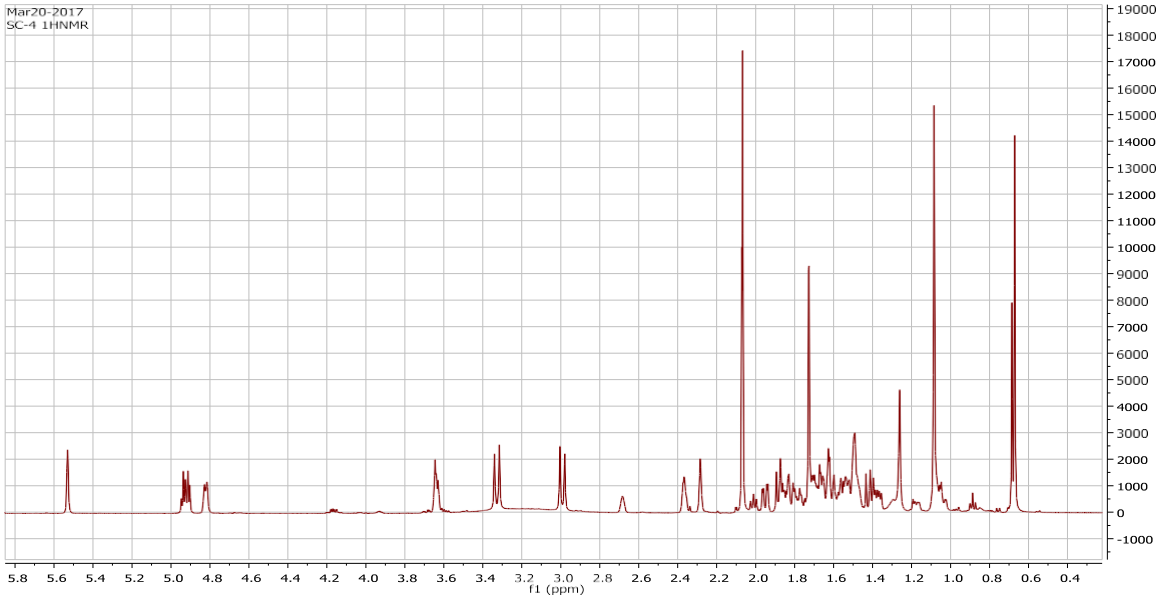


**Figure S2:** $^{1}$H-NMR (500 MHz, $CDCl_3$) Spectrum of Compound **1&2** (Sidol & Isosidol)

**Table 1:** The $^{1}H$ and $^{13}C$ NMR data of Compound **1** (Sidol) ($CDCl_3$; $\delta_H$ 500 MHz; $\delta_C$ 125 MHz)

| **C/H** | **DEPT** | **$\delta_C$** (ppm) | **$\delta_H$** (ppm), ***J*** (Hz) |
|---|---|---|---|
| 1 | $CH_2$ | 38.07 | 1.86 m, 1.06 m |
| 2 | $CH_2$ | 23.37 | 1.81 m, 1.69 m |
| 3 | CH | 74.52 | 4.93 dd (11.8, 5.3) |
| 4 | C | 41.72 | - |
| 5 | CH | 36.98 | 1.95 dd (11.6, 2.8) |
| 6 | $CH_2$ | 26.00 | 1.63† |
| 7 | CH | 74.85 | 3.63 † |
| 8 | C | 48.05 | - |
| 9 | CH | 44.63 | 2.37 |
| 10 | C | 49.98 | - |
| 11 | $CH_2$ | 17.96 | 1.56† |
| 12 | $CH_2$ | 33.60 | 1.50†, 1.70† |
| 13 | CH | 43.62 | 2.68 bs |
| 14 | $CH_2$ | 41.89 | 1.88, 1.37 |
| 15 | $CH_2$ | 45.02 | 2.28 s |
| 16 | C | 155.24 | - |
| 17 | $CH_2$ | 103.51 | 4.82 gd |
| 18 | $CH_2$ | 63.92 | 3.32 d, 2.99 d ($J_{AB}$ = 12.4) |
| 19 | $CH_3$ | 12.75 | 0.67 s |
| 20 | $CH_3$ | 18.03 | 1.08 s |
| $\underline{C}OCH_3$ | C | 171.82 | - |
| $CO\underline{C}H_3$ | $CH_3$ | 21.26 | 2.07 s |

†) *J* values could not be determined due to overlap.

**Table 2:** The $^{1}H$ and $^{13}C$ NMR data of Compound **2** (Isosidol) ($CDCl_3$; $\delta_H$ 500 MHz; $\delta_C$ 125 MHz)

| **C/H** | **DEPT** | **$\delta_C$** (ppm) | **$\delta_H$** (ppm), ***J*** (Hz) |
|---|---|---|---|
| 1 | $CH_2$ | 38.22 | 1.83†, 1.06† |
| 2 | $CH_2$ | 23.37 | 1.82†, 1.69† |
| 3 | CH | 74.57 | 4.93 dd (11.8, 5.3) |
| 4 | C | 38.51 | - |
| 5 | CH | 37.32 | 1.95 dd (11.6, 2.8) |
| 6 | $CH_2$ | 26.65 | 1.63† |
| 7 | CH | 76.84 | 3.63† |
| 8 | C | 53.20 | - |
| 9 | CH | 43.67 | 2.37 |
| 10 | C | 41.69 | - |
| 11 | $CH_2$ | 18,49 | 1.49† |
| 12 | $CH_2$ | 24.89 | 1.50†, 1.70† |
| 13 | CH | 45.01 | 2.31gs |
| 14 | $CH_2$ | 38.38 | 1.88, 1.37 |
| 15 | CH | 130.16 | 5.53 s |
| 16 | C | 143.68 | - |
| 17 | $CH_3$ | 15.48 | 1.72 |
| 18 | $CH_2$ | 63.92 | 3.32 d, 2.99 d ($J_{AB}$ = 12.4) |
| 19 | $CH_3$ | 12.89 | 0.69 s |
| 20 | $CH_3$ | 18.00 | 1.08 s |
| $\underline{C}OCH_3$ | C | 171.85 | - |
| $CO\underline{C}H_3$ | $CH_3$ | 21.26 | 2.07 s |

†) *J* values could not be determined due to overlap.

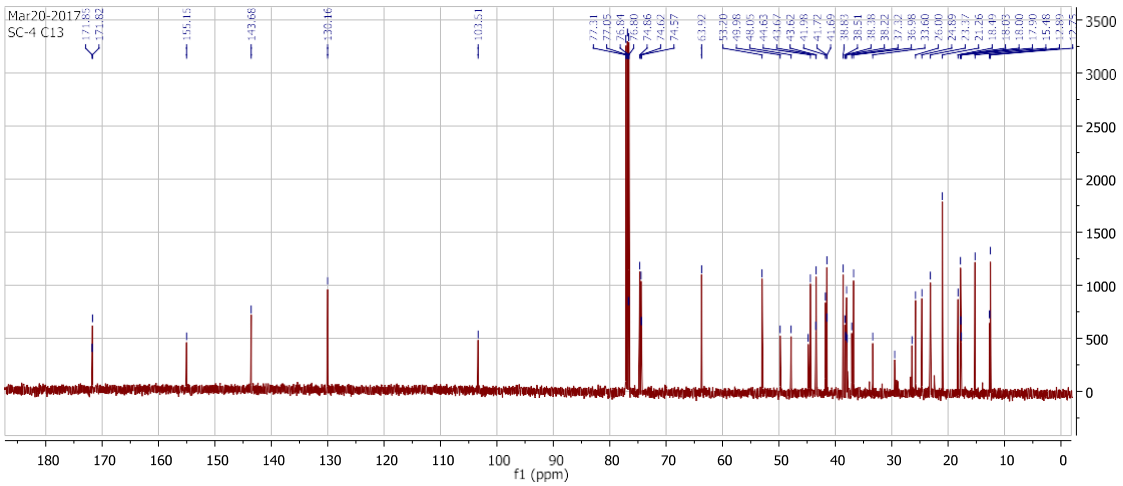


**Figure S3:** $^{13}$C-NMR (125 MHz, $CDCl_3$) Spectrum of Compound **1&2** (Sidol & Isosidol)

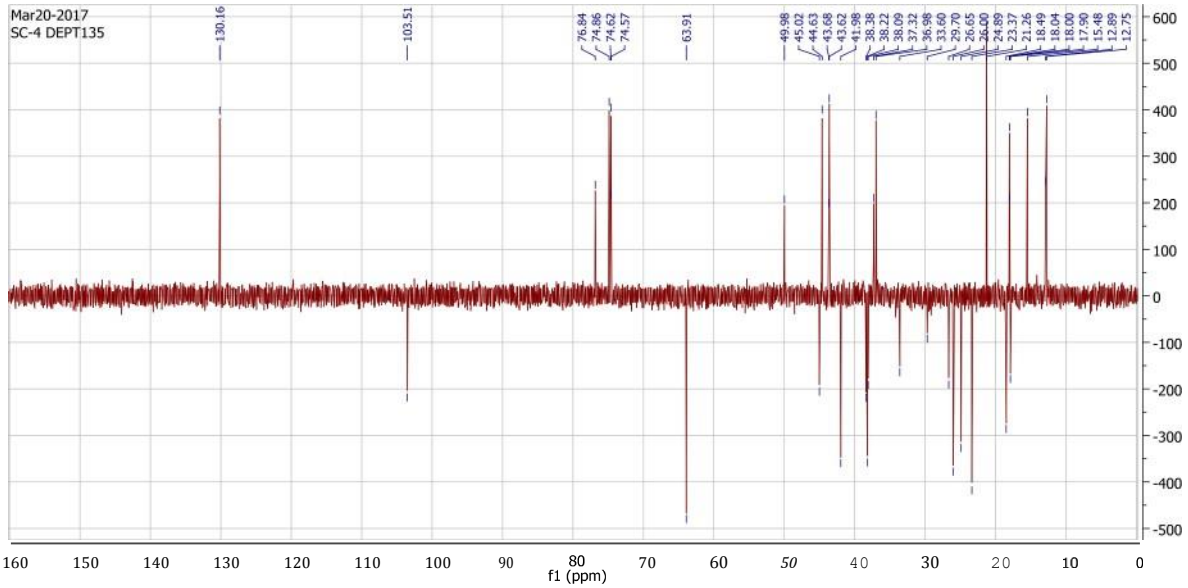


**Figure S4:** DEPT-135 Spectrum of Compound **1&2** (Sidol & Isosidol)

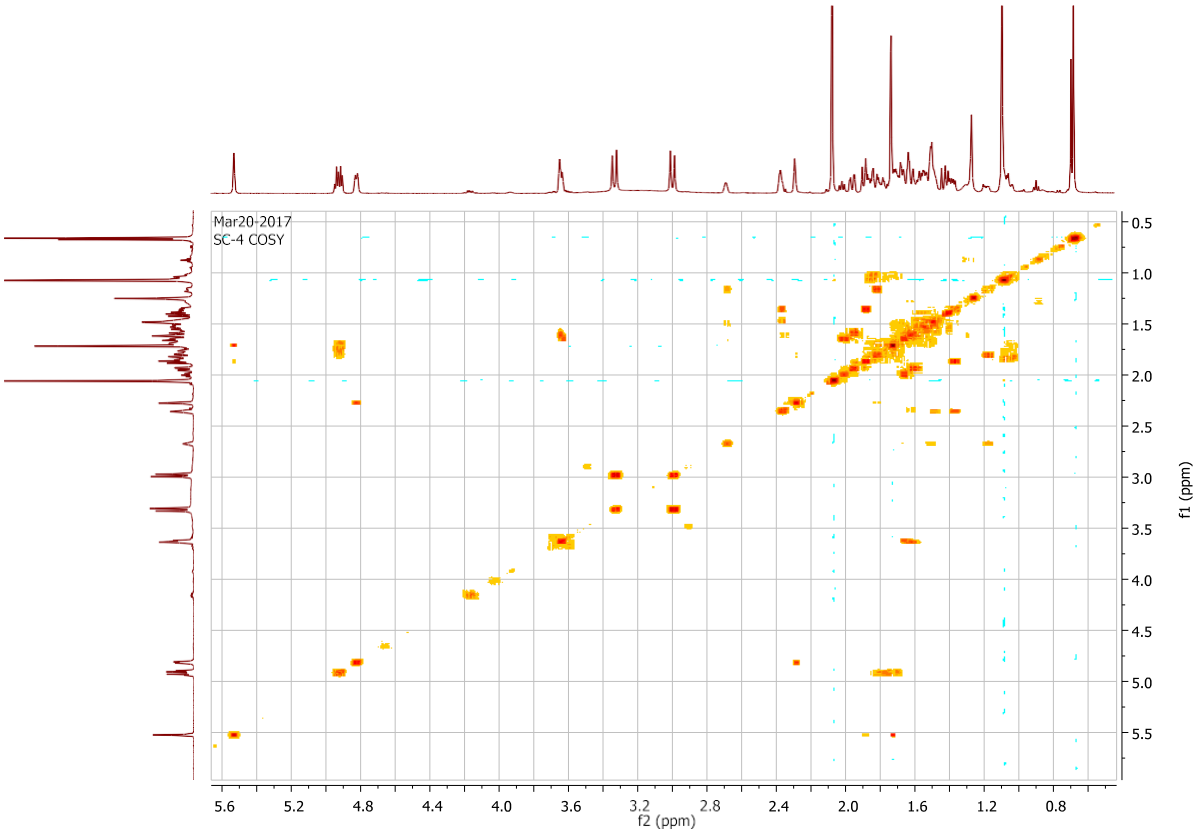


**Figure S5:** COSY Spectrum of Compound **1&2** (Sidol & Isosidol)

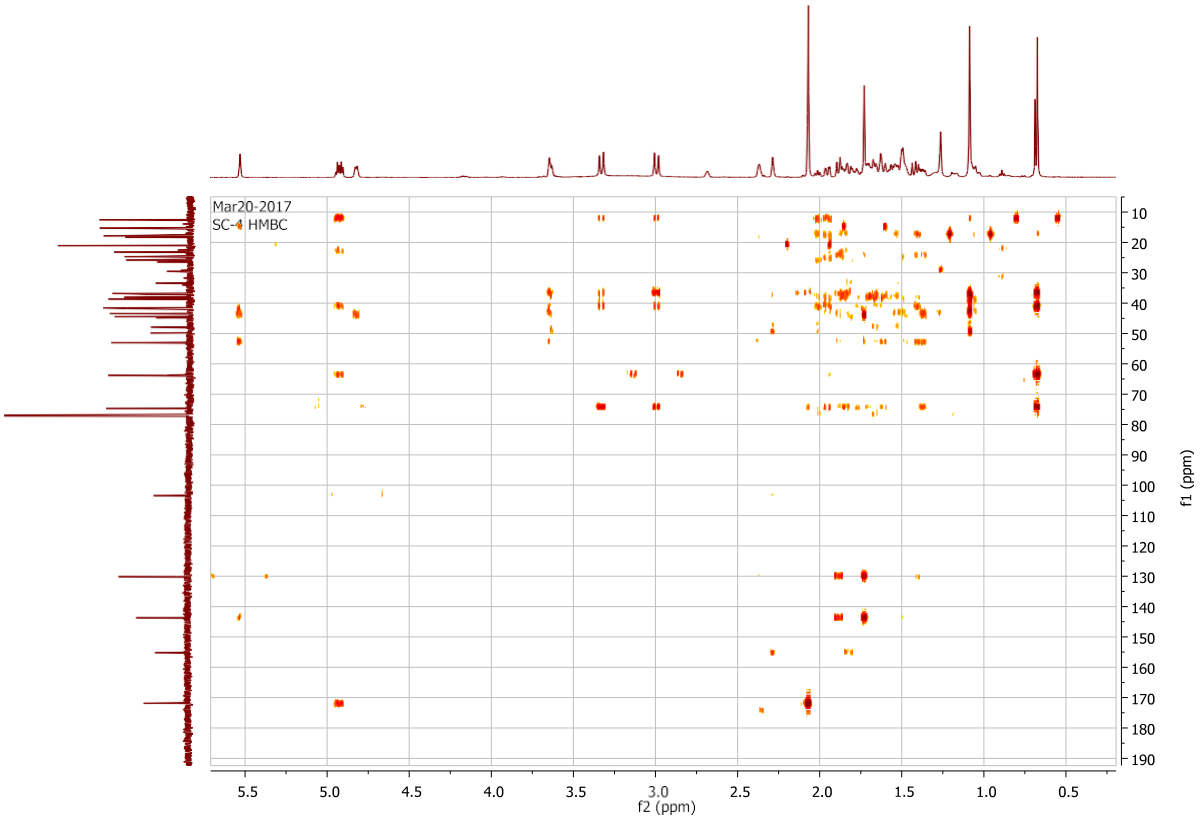


**Figure S6:** HMBC Spectrum of Compound **1&2** (Sidol & Isosidol)

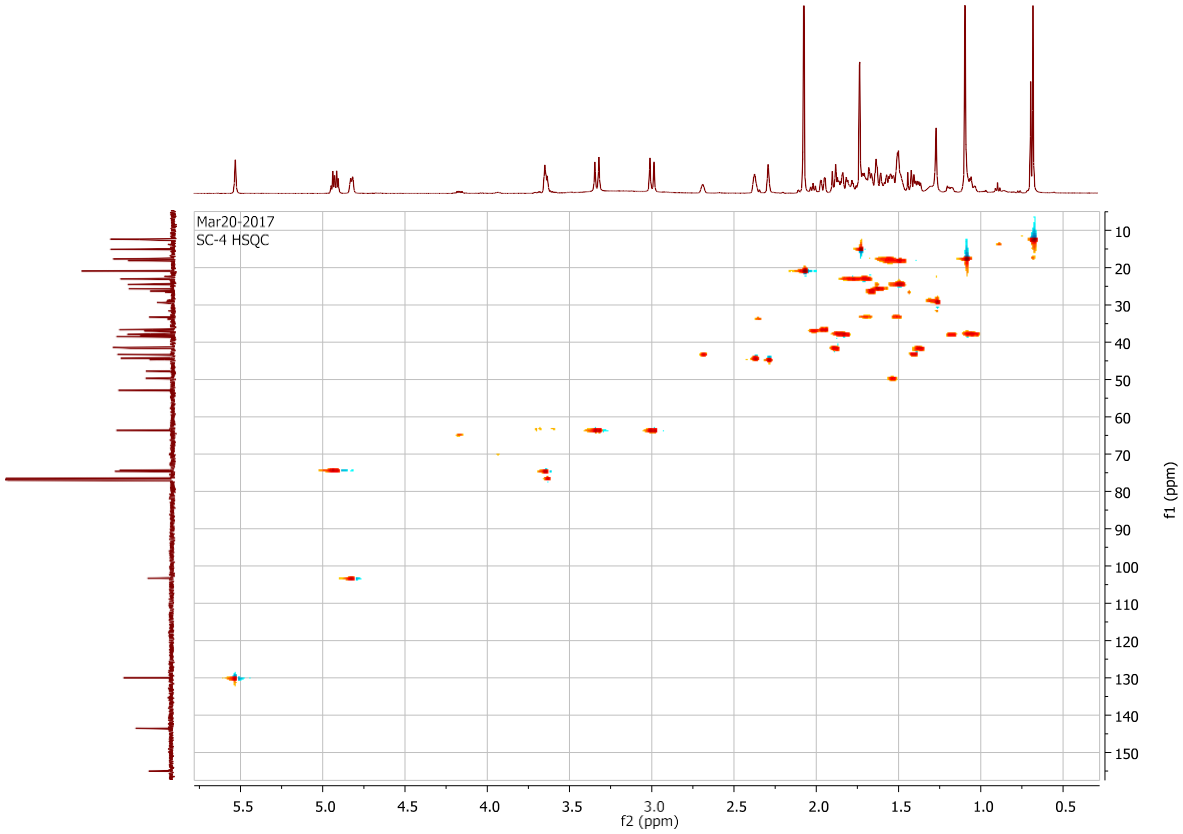


**Figure S7:** HSQC Spectrum of Compound **1&2** (Sidol & Isosidol)

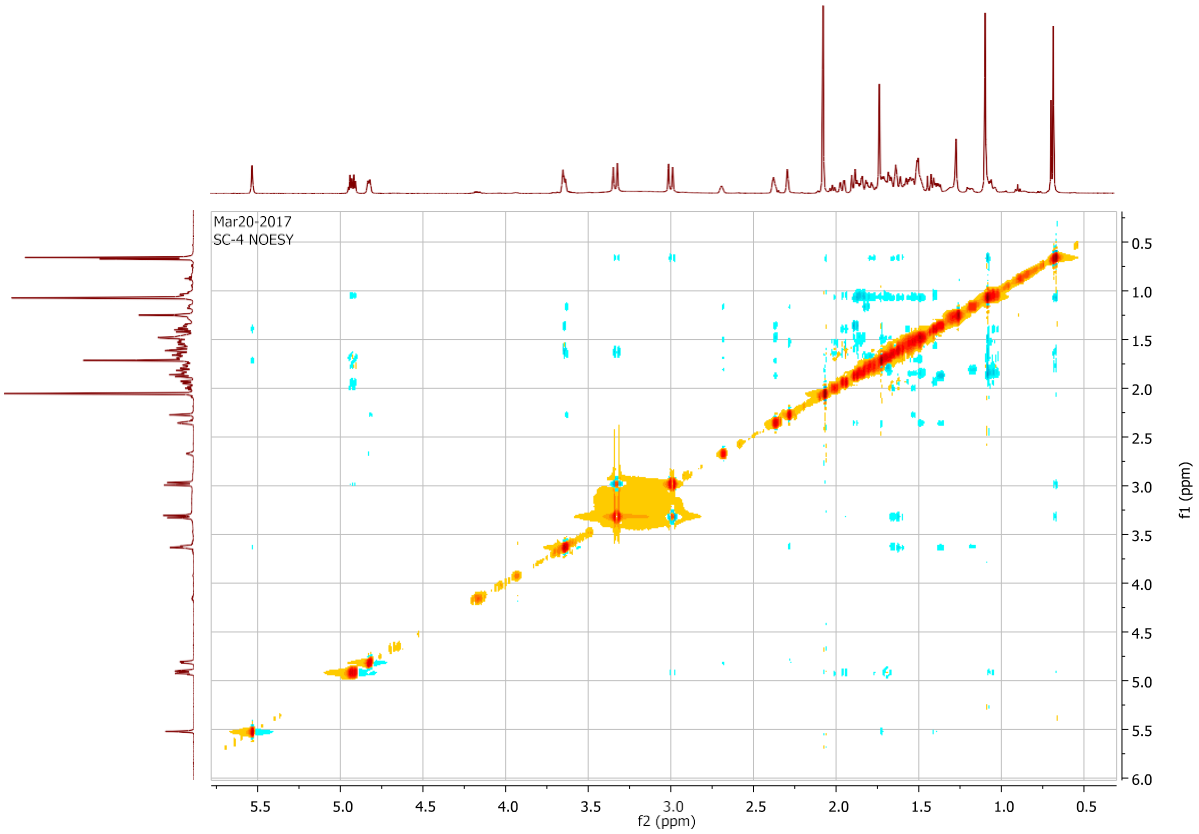


**Figure S8:** NOESY Spectrum of Compound **1&2** (Sidol & Isosidol)

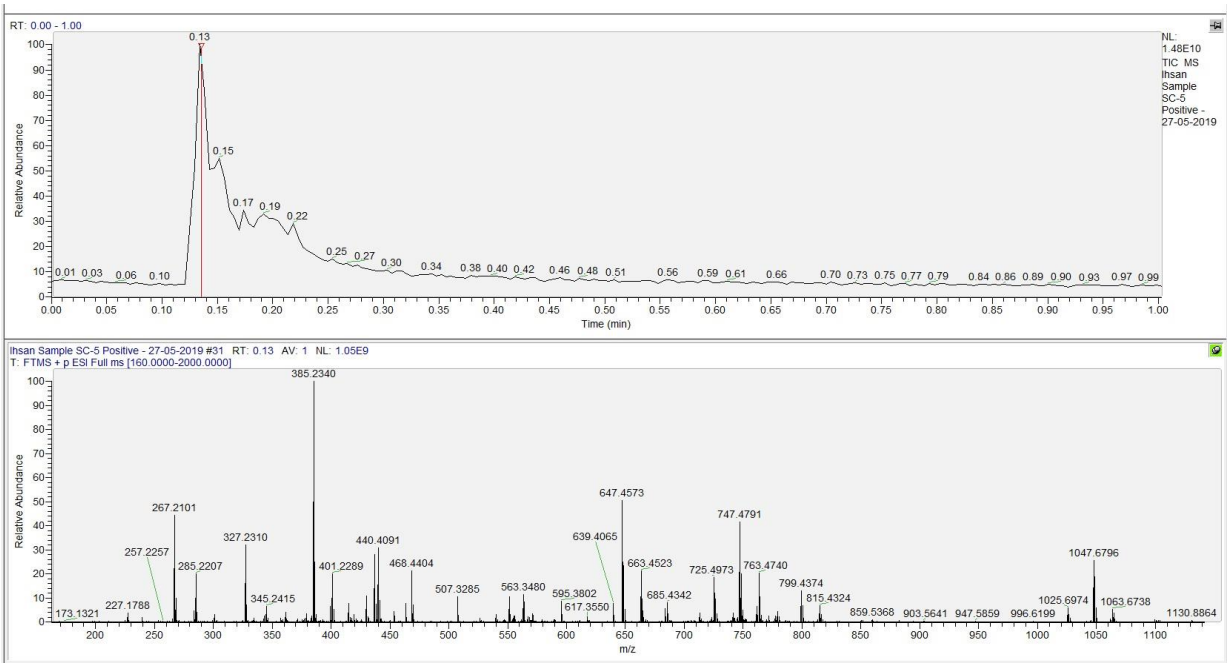


**Figure S9:** Positive- ion HRLCMS-MS Spectrum of Compound **3&4** (Linearol & Isolinearol)

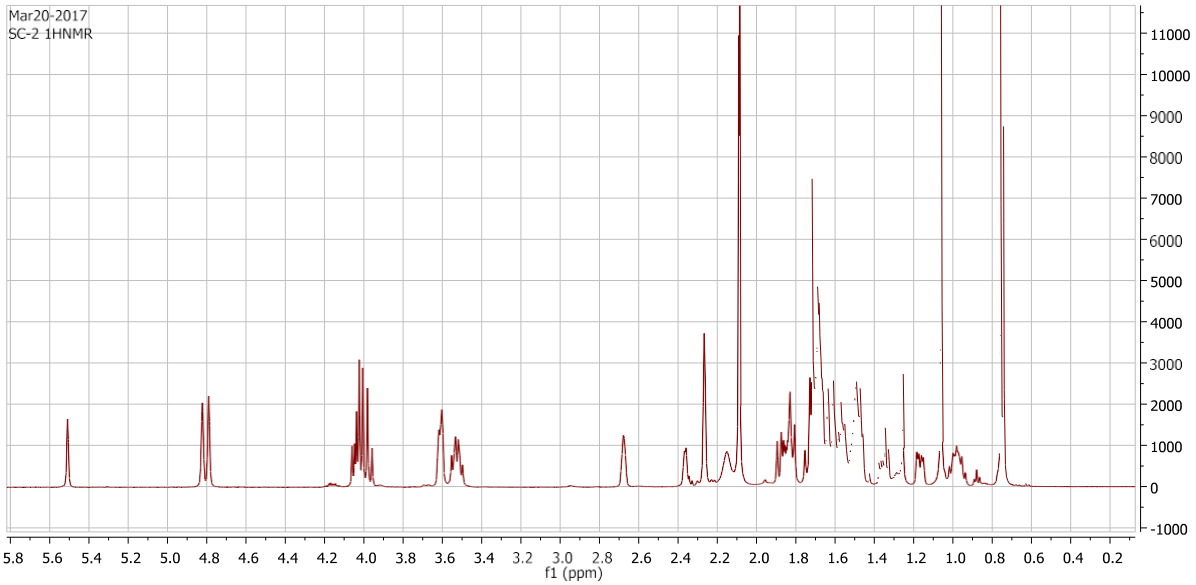


**Figure S10:** $^{1}$H-NMR (500 MHz, $CDCl_3$) Spectrum of Compound **3&4** (Linearol & Isolinearol)

**Table 3:** The $^{1}H$ and $^{13}C$ NMR data of Compound **3** (Linearol) ($CDCl_3$; $\delta_H$ 500 MHz; $\delta_C$ 125 MHz)

| **C/H** | **DEPT** | **$\delta_C$** (ppm) | **$\delta_H$** (ppm), ***J*** (Hz) |
|---|---|---|---|
| 1 | $CH_2$ | 38.41 | 1.85†, 0.98 m |
| 2 | $CH_2$ | 26.47 | 1.67† |
| 3 | CH | 74.21 | 3.52 dd (8.0, 10.0) |
| 4 | C | 41.79 | - |
| 5 | CH | 38.14 | 1.76† |
| 6 | $CH_2$ | 27.32 | 1.70†, 1.64† |
| 7 | CH | 76.82 | 3.60 gs |
| 8 | C | 47.94 | - |
| 9 | CH | 50.21 | 1.46† |
| 10 | C | 38.14 | - |
| 11 | $CH_2$ | 17.83 | 1.56† |
| 12 | $CH_2$ | 33.52 | 1.68†, 1.49† |
| 13 | CH | 42.05 | 2.63 gs |
| 14 | $CH_2$ | 38.26 | 1.82 gd (11.2), 1.17 dd (11.2, 4.8) |
| 15 | $CH_2$ | 45.04 | 2.27 gs |
| 16 | C | 155.01 | - |
| 17 | $CH_2$ | 103.55 | 4.79 gs, 4.82 gs |
| 18 | $CH_2$ | 66.09 | 3.99 d (11.6), 4.04 d (11.6) |
| 19 | $CH_3$ | 11.96 | 0.76 s |
| 20 | $CH_3$ | 17.96 | 1.05 s |
| $\underline{C}OCH_3$ | C | 171.91 | - |
| $CO\underline{C}H_3$ | $CH_3$ | 21.20 | 2.09 s |

†) *J* values could not be determined due to overlap.

**Table 4:** The $^{1}H$ and $^{13}C$ NMR data of Compound **4** (Isolinearol) ($CDCl_3$; $\delta_H$ 500 MHz; $\delta_C$ 125 MHz)

| C/H | DEPT | $\delta_C$ ppm | $\delta_H$ ppm, *J* (Hz) |
|---|---|---|---|
| 1 | $CH_2$ | 38.14 | 1.85†, 0.98† |
| 2 | $CH_2$ | 26.71 | 1.70 – 1.60† |
| 3 | CH | 72.18 | 3.52† |
| 4 | C | 41.80 | - |
| 5 | CH | 37.00 | 1.76† |
| 6 | $CH_2$ | 26.47 | 1.70 – 1.60† |
| 7 | CH | 74.80 | 3.61 gs |
| 8 | C | 53.00 | - |
| 9 | CH | 43.83 | 1.33† |
| 10 | C | 38.41 | - |
| 11 | $CH_2$ | 18.04 | 1.50† |
| 12 | $CH_2$ | 24.83 | 1.48† |
| 13 | CH | 44.57 | 2.36 gs |
| 14 | $CH_2$ | 42.05 | 1.87†, 1.32† |
| 15 | CH | 130.04 | 5.51 s |
| 16 | C | 143.85 | - |
| 17 | $CH_3$ | 15.47 | 1.72 s |
| 18 | $CH_2$ | 66.05 | 4.04 d (11.0), 3.97 d (11.0) |
| 19 | $CH_3$ | 11.82 | 0.74 s |
| 20 | $CH_3$ | 18.04 | 1.05 s |
| $\underline{C}OCH_3$ | C | 171.91 | - |
| $CO\underline{C}H_3$ | $CH_3$ | 21.20 | 2.09 |

†) *J* values could not be determined due to overlap.

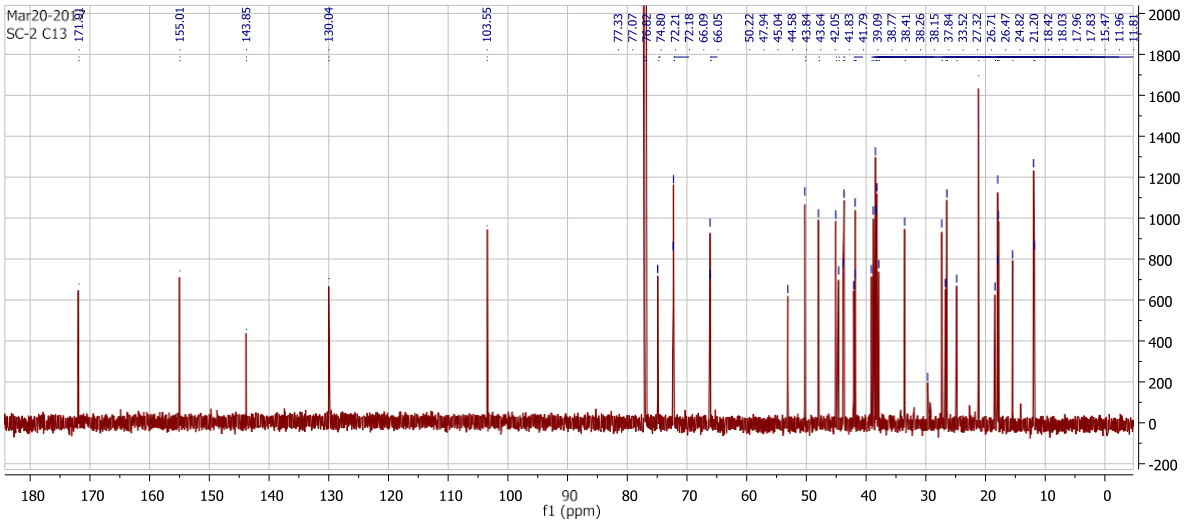


**Figure S11:** $^{13}$C-NMR (125 MHz, $CDCl_3$) Spectrum of Compound **3&4** (Linearol & Isolinearol)

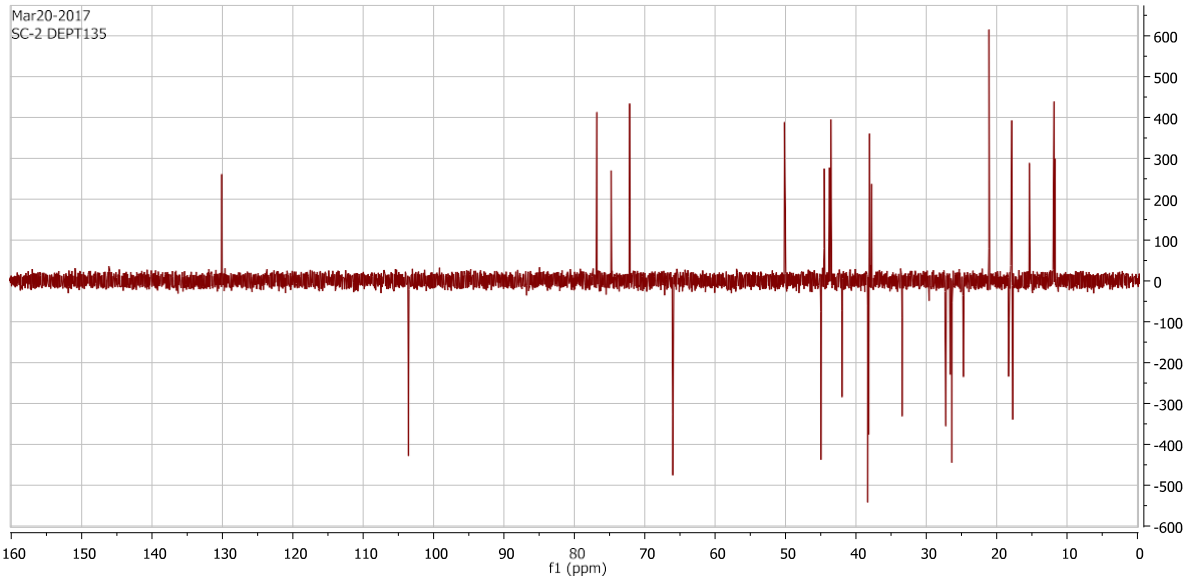


**Figure S12:** DEPT-135 Spectrum of Compound **3&4** (Linearol & Isolinearol)

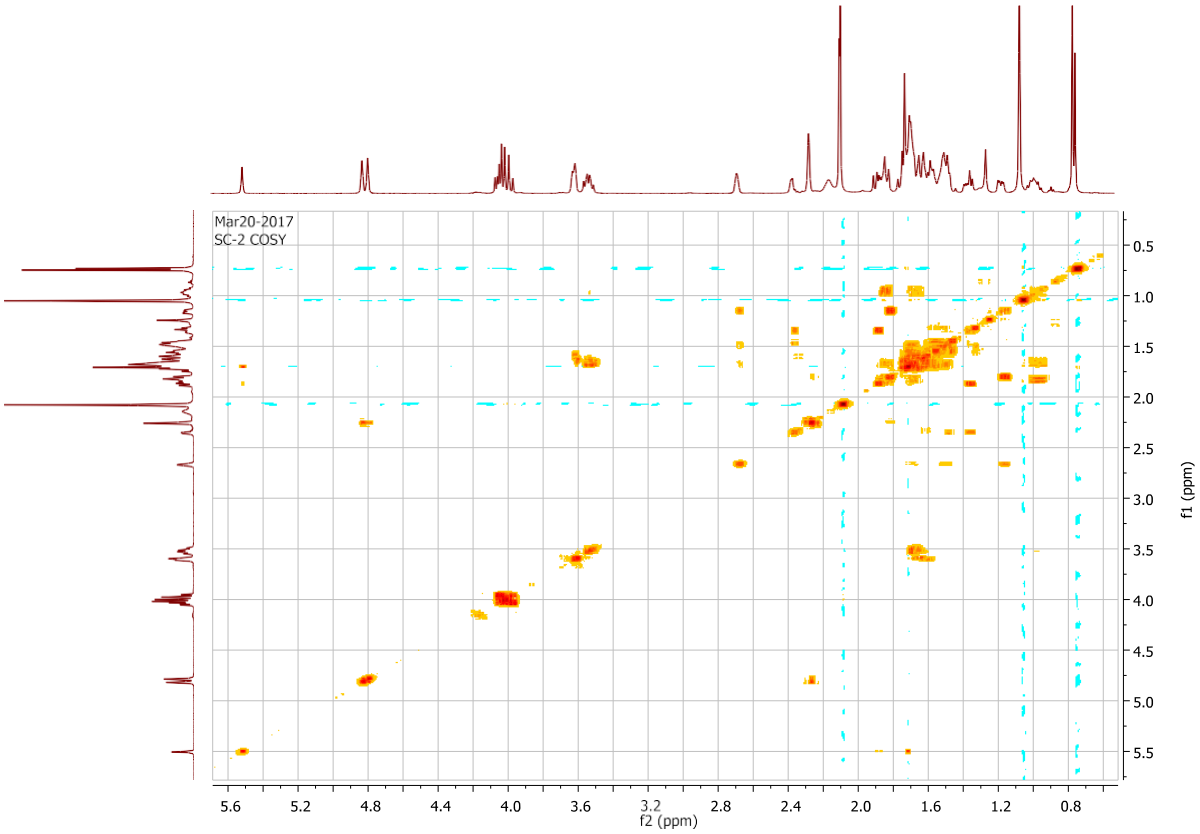


**Figure S13:** COSY Spectrum of Compound **3&4** (Linearol & Isolinearol)

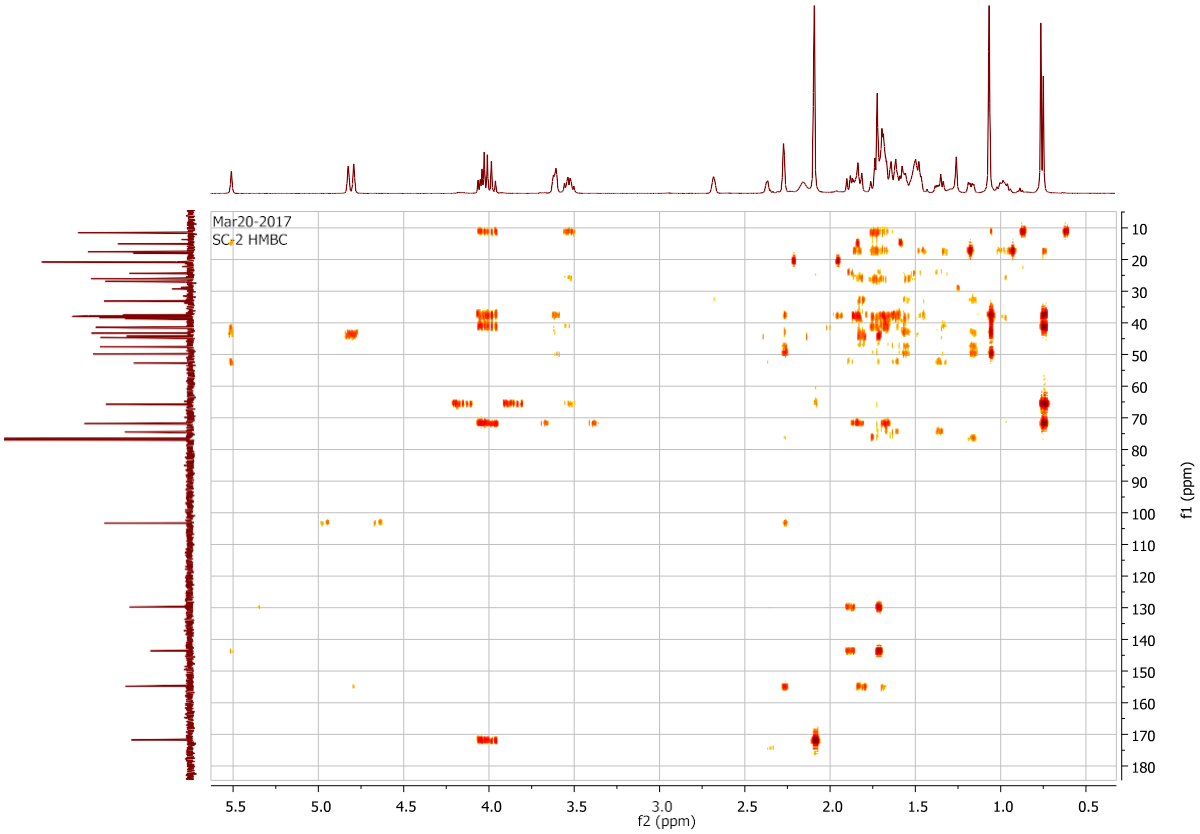


**Figure S14:** HMBC Spectrum of Compound **3&4** (Linearol & Isolinearol)

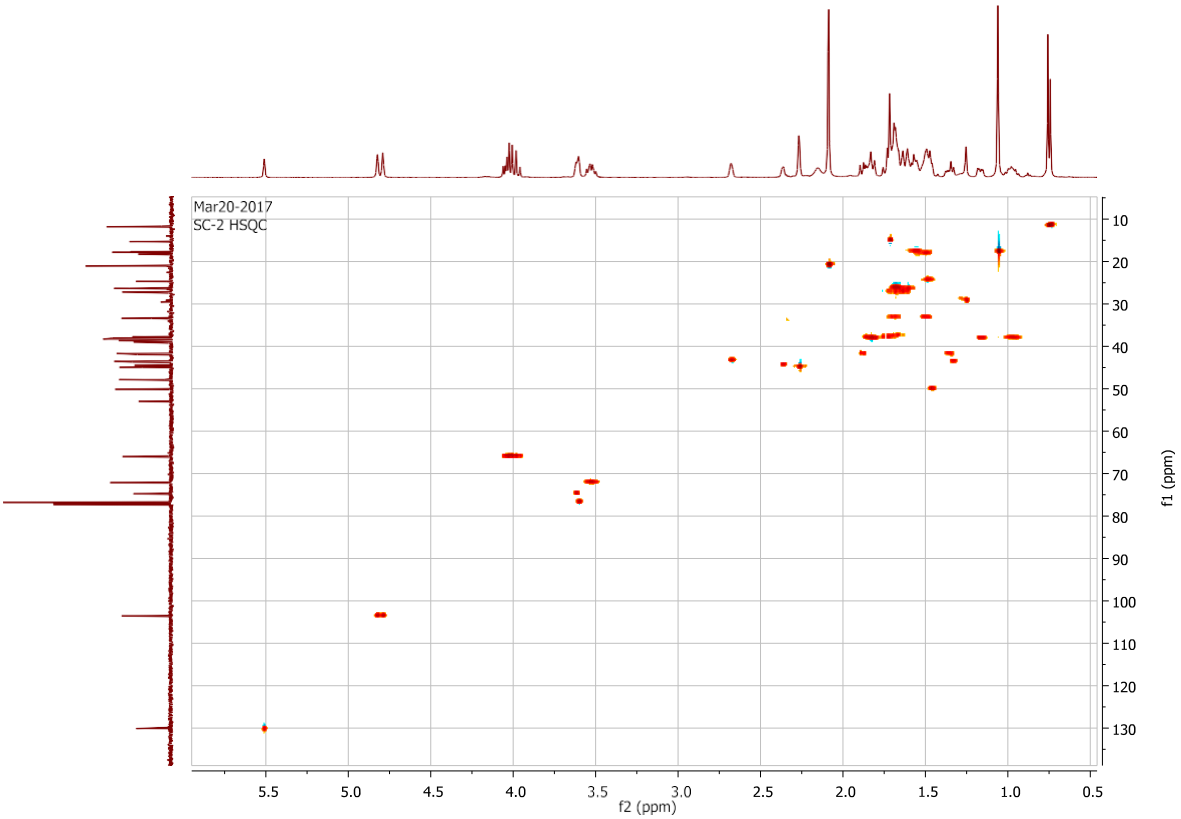


**Figure S15:** HSQC Spectrum of Compound **3&4** (Linearol & Isolinearol)

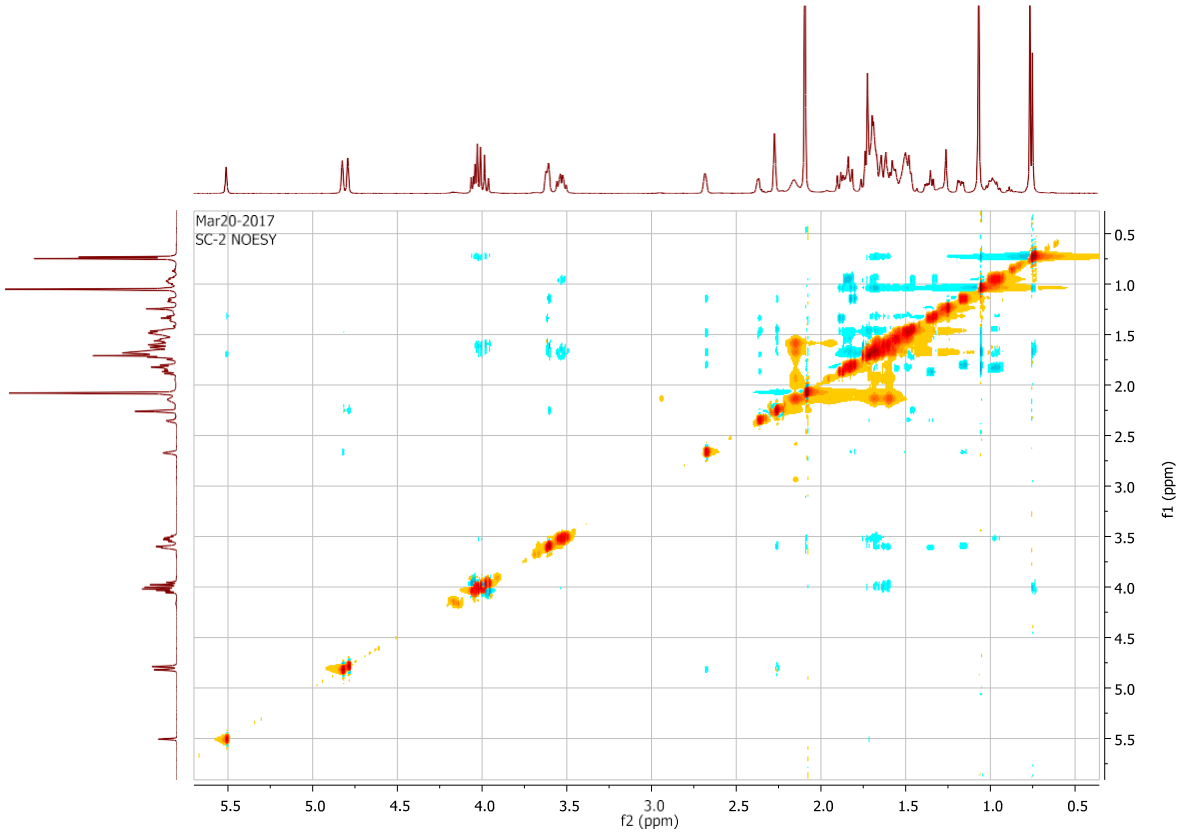


**Figure S16:** NOESY Spectrum of Compound **3&4** (Linearol & Isolinearol)

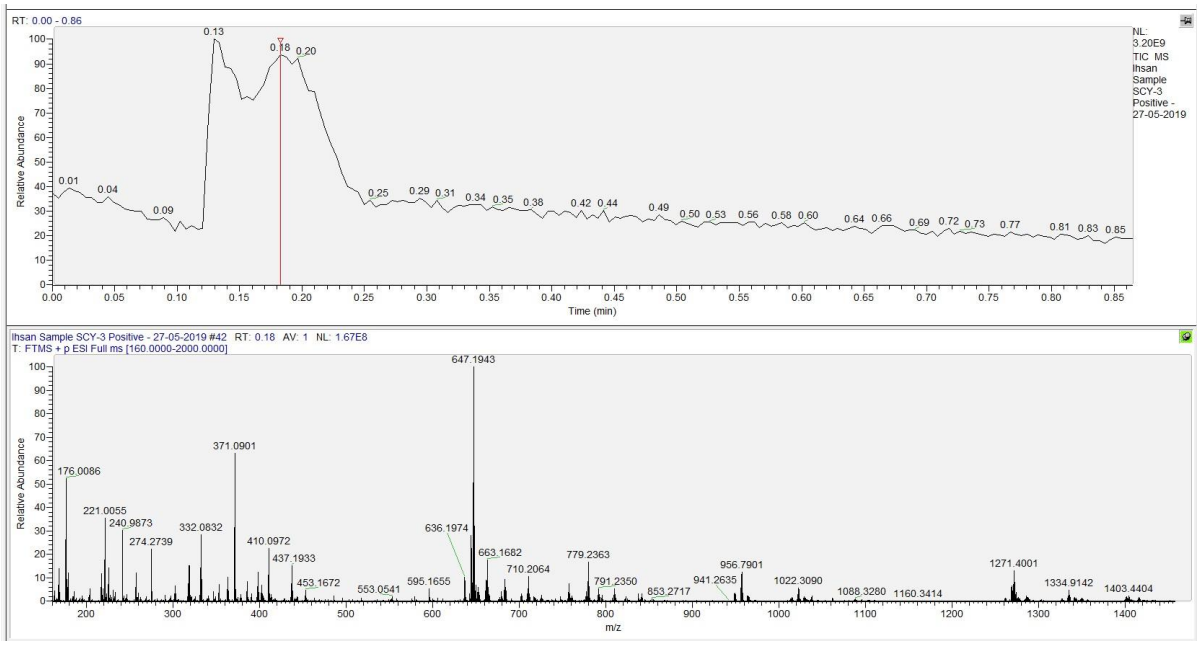


**Figure S17:** Positive- ion HRLCMS-MS Spectrum of Compound **5** (Verbascoside)

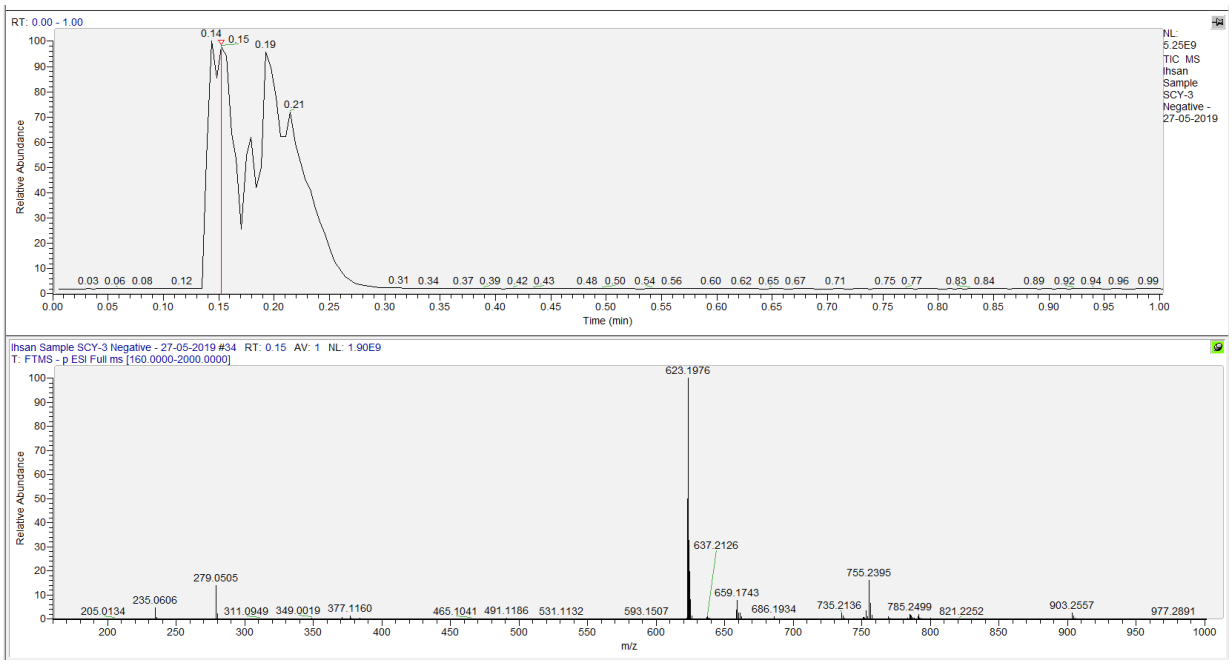


**Figure S18:** Negative- ion HRLCMS-MS Spectrum of Compound **5** (Verbascoside)

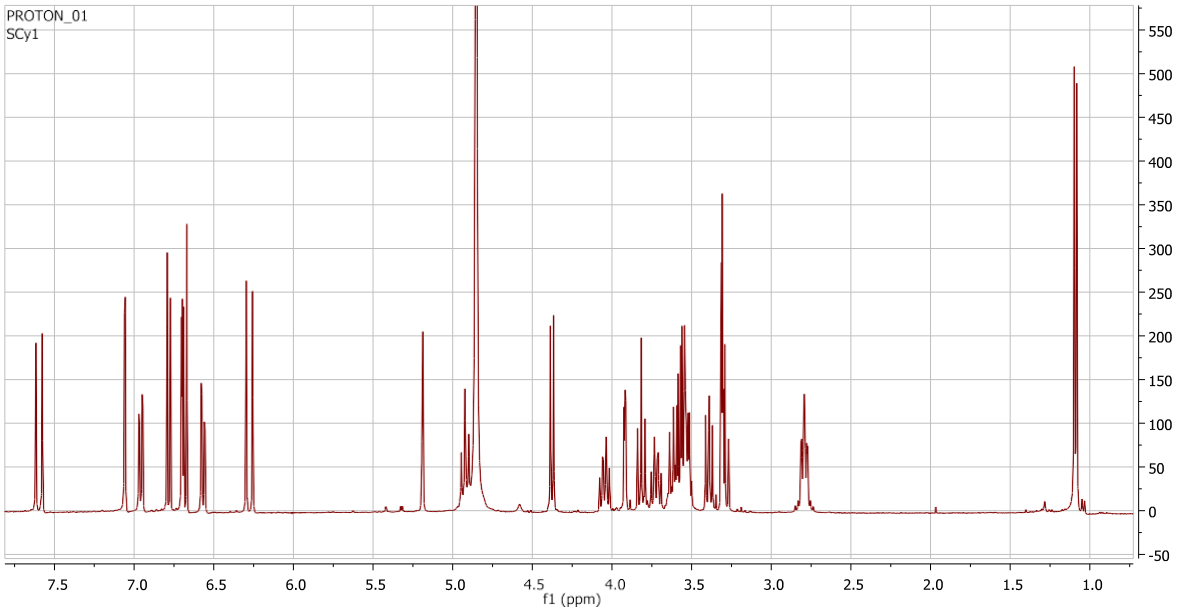


**Figure S19:** $^{1}$H-NMR (500 MHz, $CD_3OD$) Spectrum of Compound **5** (Verbascoside)

**Table 5:** The $^{1}H$ and $^{13}C$ NMR data of Compound **5** (Verbascoside) ($CD_3OD$; $\delta_H$ 500 MHz; $\delta_C$ 125 MHz)

| C/H | DEPT | $\delta_C$ (ppm) | $\delta_H$ (ppm), *J* (Hz) |
|---|---|---|---|
| Phenylethyl alcohol 1 | C | 131.5 | - |
| 2 | CH | 117.2 | 6.70 d (2.0) |
| 3 | C | 146.7 | - |
| 4 | C | 144.3 | - |
| 5 | CH | 116.4 | 6.68 d (8.1) |
| 6 | CH | 121.3 | 6.57 dd (8.1 / 2.0) |
| α | $CH_2$ | 72.2 | 4.04 ddd "dt" (7.0, 8.3)<br>3.72 ddd "dt" (7.0, 8.3) |
| β | $CH_2$ | 36.5 | 2.79 ddd "dt" (7.0, 8.3) |
| Glucose 1' | CH | 104.3 | 4.38 d (8.0) |
| 2' | CH | 76.1 | 3.39 dd (8.0/ 9.0) |
| 3' | CH | 81.7 | 3.80 dd"t" (9.0) |
| 4' | CH | 70.5 | 4.92 dd"t" (9.0) |
| 5' | CH | 74.6 | 3.53† |
| 6' | $CH_2$ | 62.4 | 3.62†, 3.52† |
| Rhamnose 1" | CH | 103.1 | 5.19 d (1.7) |
| 2" | CH | 72.2 | 3.92 dd (1.7, 3.2) |
| 3" | CH | 71.9 | 3.58 dd (3.2, 9.6) |
| 4" | CH | 73.7 | 3.29 dd"t" (9.6) |
| 5" | CH | 70.4 | 3.55† |
| 6" | $CH_3$ | 18.4 | 1.09 d (6.2 |
| Caffeic acid 1'" | C | 127.7 | - |
| 2'" | CH | 115.3 | 7.05 d (2.0) |
| 3'" | C | 146.9 | - |
| 4'" | C | 149.9 | - |
| 5'" | CH | 116.6 | 6.78 d (8.2) |
| 6'" | CH | 123.2 | 6.95 dd (8.2 / 2.0) |
| α' | CH | 114.8 | 6.27 d (16.0) |
| β' | CH | 148.1 | 7.58 d (16.0) |
| C=O | C | 168.3 | - |

†) *J* values could not be determined due to overlap.

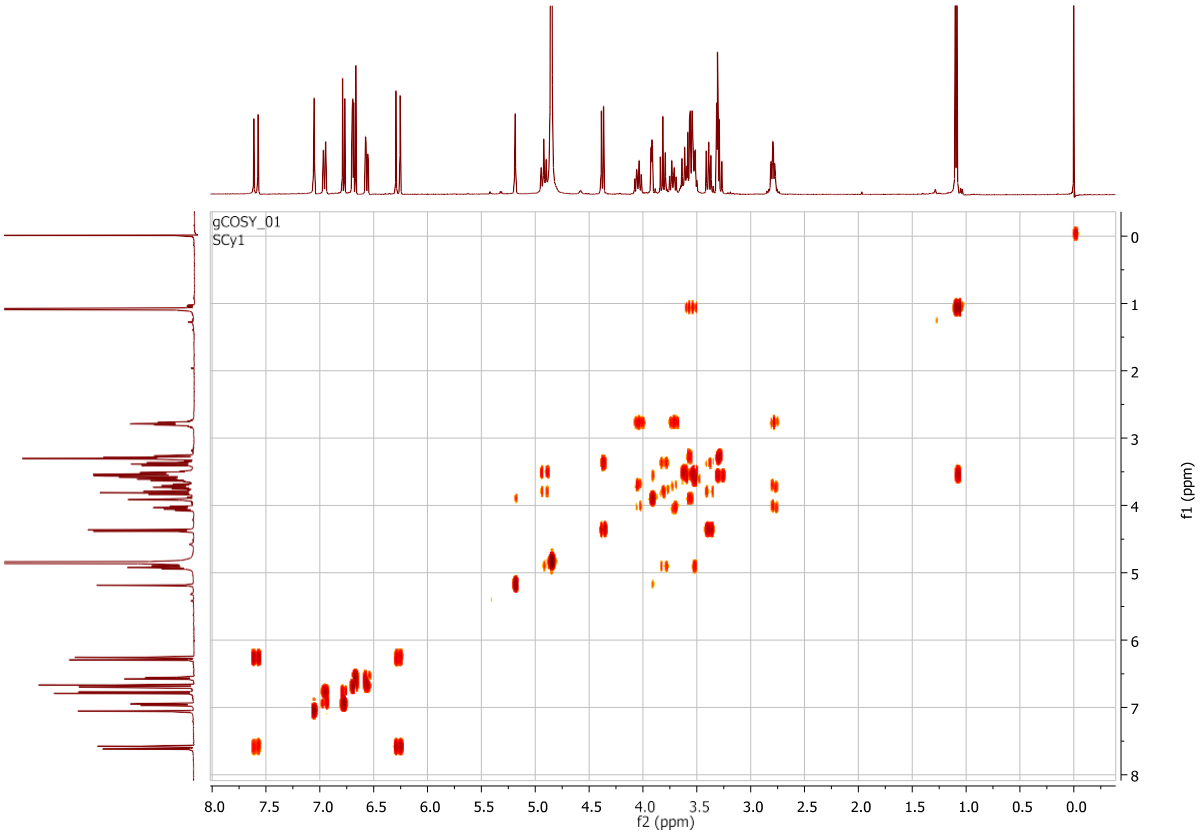


**Figure S20:** COSY Spectrum of Compound **5** (Verbascoside)

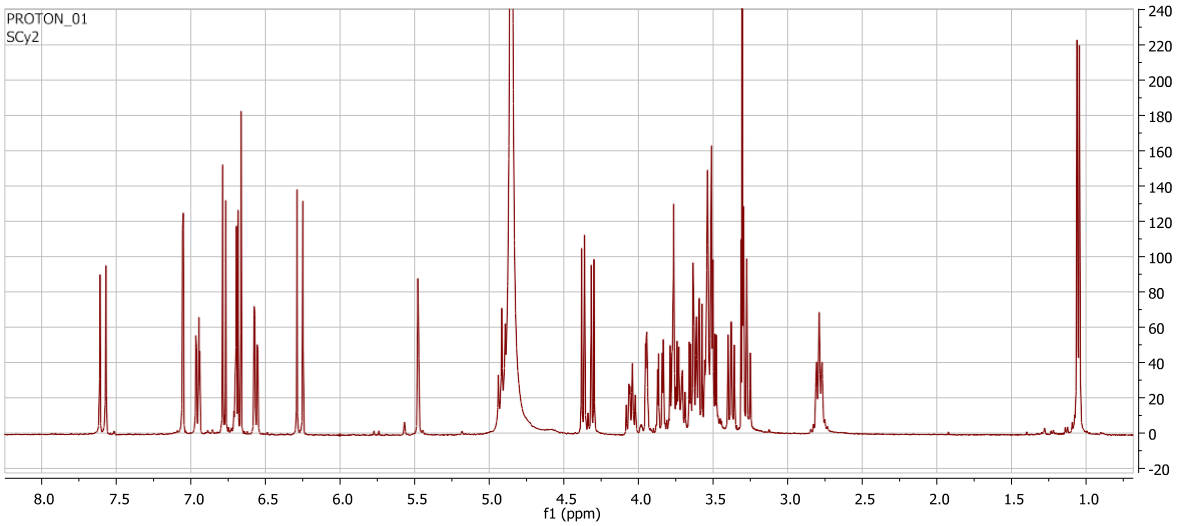


**Figure S21:** $^{1}$H-NMR (500 MHz, $CD_3OD$) Spectrum of Compound **6** (Lavandulifolioside)

**Table 6:** The $^{1}H$ and $^{13}C$ NMR data of Compound **6** (Lavandulifolioside) ($CD_3OD$; $\delta_H$ 500 MHz; $\delta_C$ 125 MHz)

| **C/H** | **DEPT** | **$\delta_C$** (ppm) | **$\delta_H$** (ppm), ***J*** (Hz) |
|---|---|---|---|
| Phenylethyl alcohol 1 | C | 131.5 | - |
| 2 | CH | 116.5 | 7.05 d (2.0) |
| 3 | C | 146.1 | - |
| 4 | C | 144.7 | - |
| 5 | CH | 117.1 | 6.77 d (8.0) |
| 6 | CH | 121.3 | 6.95 dd (8.0 / 2.0) |
| α | $CH_2$ | 72.3 | 4.04 ddd "dt" (7.0, 8.3)<br>3.72 ddd "dt" (7.0, 8.3) |
| β | $CH_2$ | 36.6 | 2.79 t (7.4) |
| Glucose 1' | CH | 104.2 | 4.37 d (8.0) |
| 2' | CH | 76.0 | 3.38 dd (7.9 / 9.0) |
| 3' | CH | 82.4 | 3.76 dd"t" (9.0) |
| 4' | CH | 70.3 | 4.92 dd"t" (9.0) |
| 5' | CH | 76.0 | 3.52† |
| 6' | $CH_2$ | 62.3 | 3.60†, 3.51† |
| Rhamnose 1" | CH | 102.0 | 5.48 d (1.7) |
| 2" | CH | 82.80 | 3.94dd (1.7, 3.4) |
| 3" | CH | 71.9 | 3.64 dd (3.4 / 9.5) |
| 4" | CH | 74.2 | 3.27 dd"t" (9.5) |
| 5" | CH | 70.5 | 3.53† |
| 6" | $CH_3$ | 18.4 | 1.05 d (6.2) |
| Arabinose 1"' | CH | 107.5 | 4.31 d (7.3) |
| 2"' | CH | 72.8 | 3.59 dd (7.3, 9.3) |
| 3"' | CH | 74.5 | 3.49 dd (9.3, 3.5) |
| 4"' | CH | 69.8 | 3.76† |
| 5"' | $CH_2$ | 67.3 | 3.85 dd (12.6, 2.6), 3.51† |
| Caffeic acid 1"" | C | 127.6 | - |
| 2"" | CH | 114.7 | 7.05 d (2.0) |
| 3"" | C | 146.8 | - |
| 4"" | C | 149.8 | - |
| 5"" | CH | 116.3 | 6.77d (8.2) |
| 6"" | CH | 123.2 | 6.95 dd (8.2 / 2.0) |
| α' | CH | 115.2 | 6.27 d (15.9) |
| β' | CH | 148.0 | 7.59 d (15.9) |
| C=O | C | 168.3 | - |

†) *J* values could not be determined due to overlap.

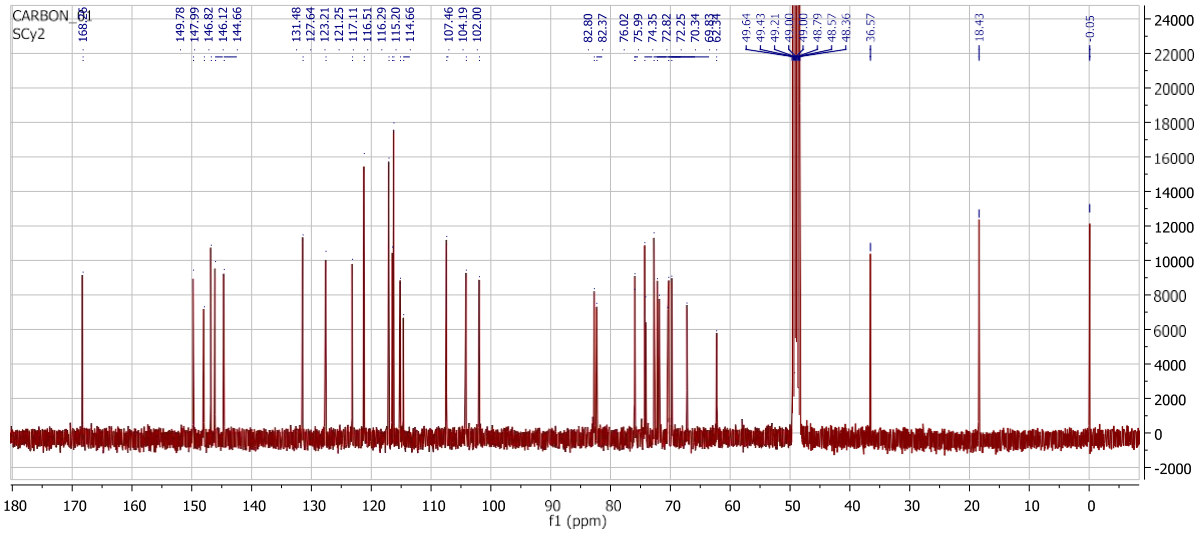


**Figure S22:** $^{13}$C-NMR (125 MHz, $CD_3OD$) Spectrum of Compound **6** (Lavandulifolioside)

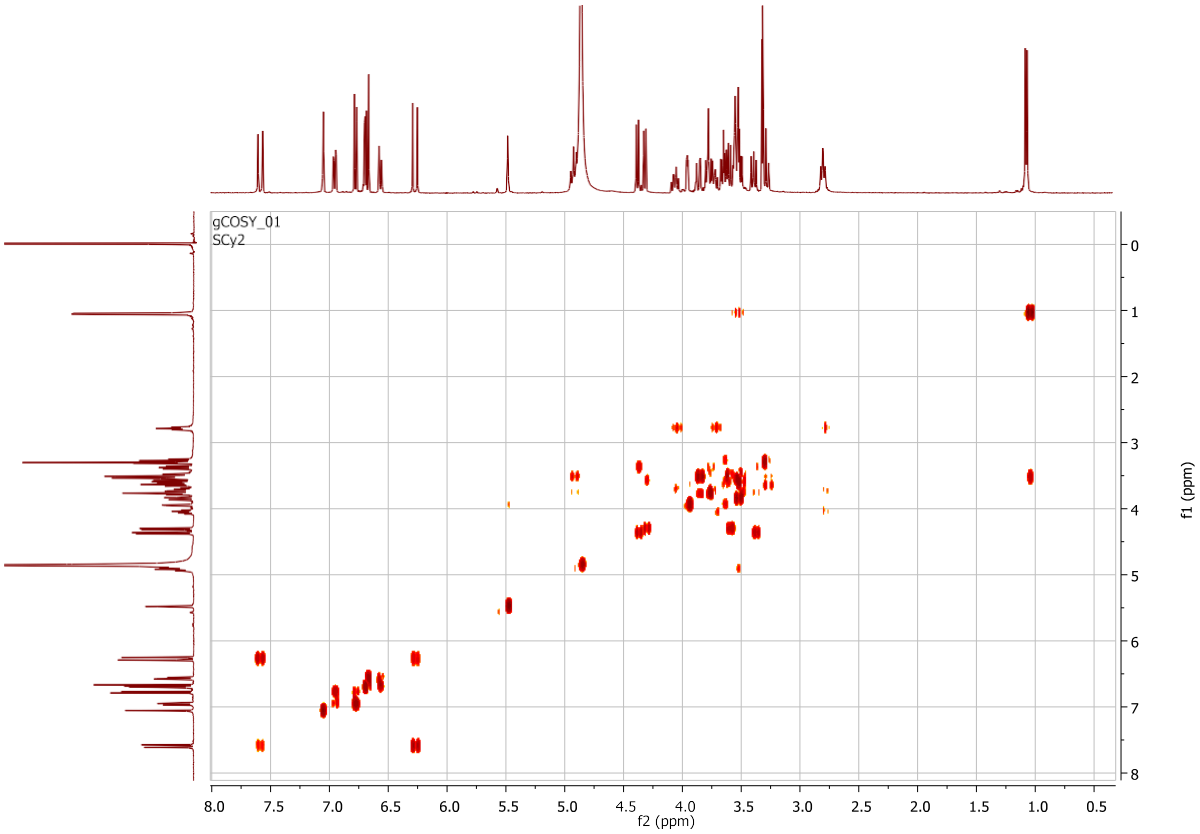


**Figure S23:** COSY Spectrum of Compound **6** (Lavandulifolioside)

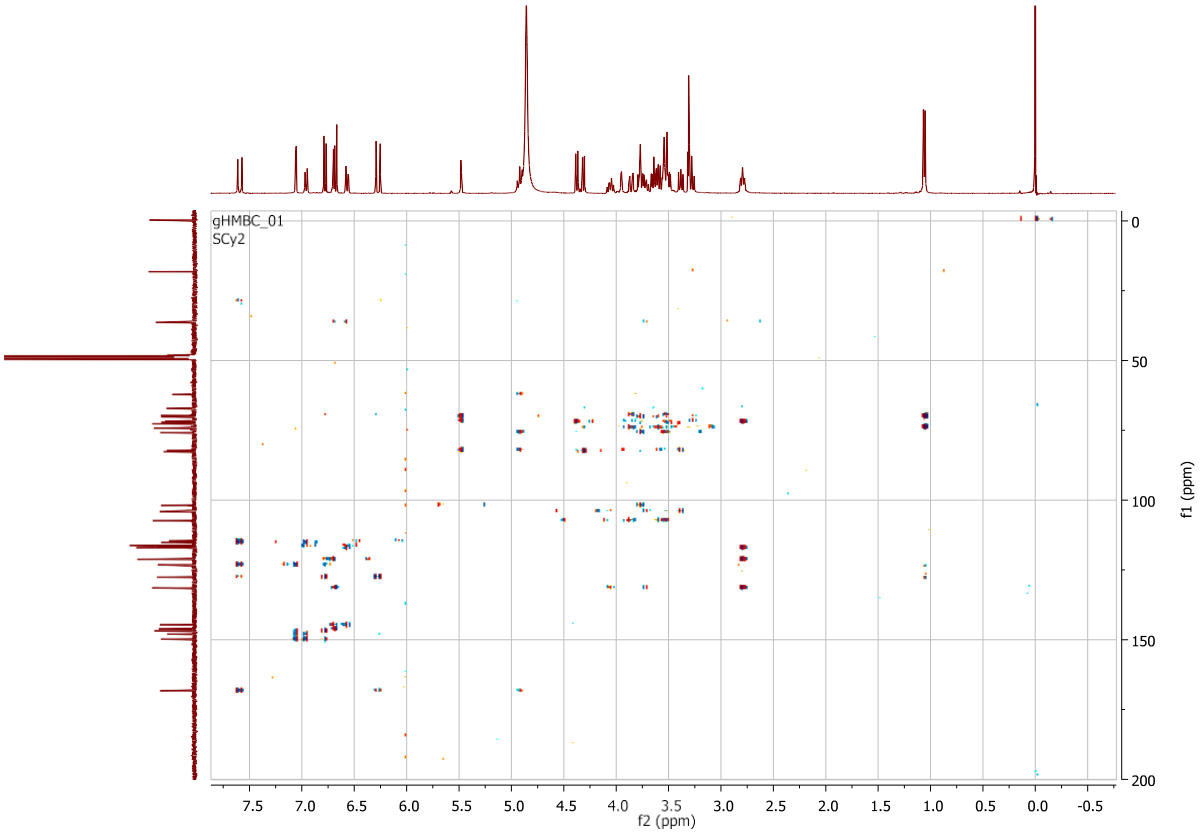


**Figure S24:** HMBC Spectrum of Compound **6** (Lavandulifolioside)

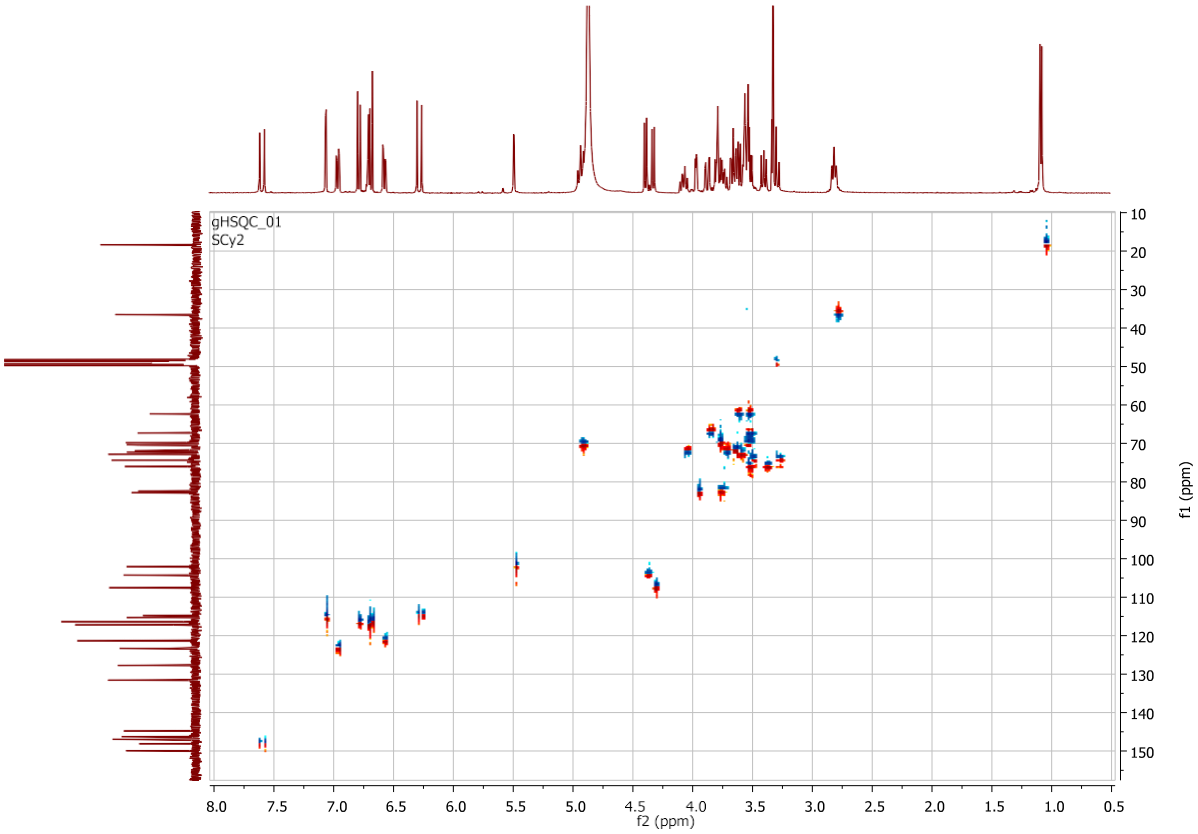


**Figure S25:** HSQC Spectrum of Compound **6** (Lavandulifolioside)

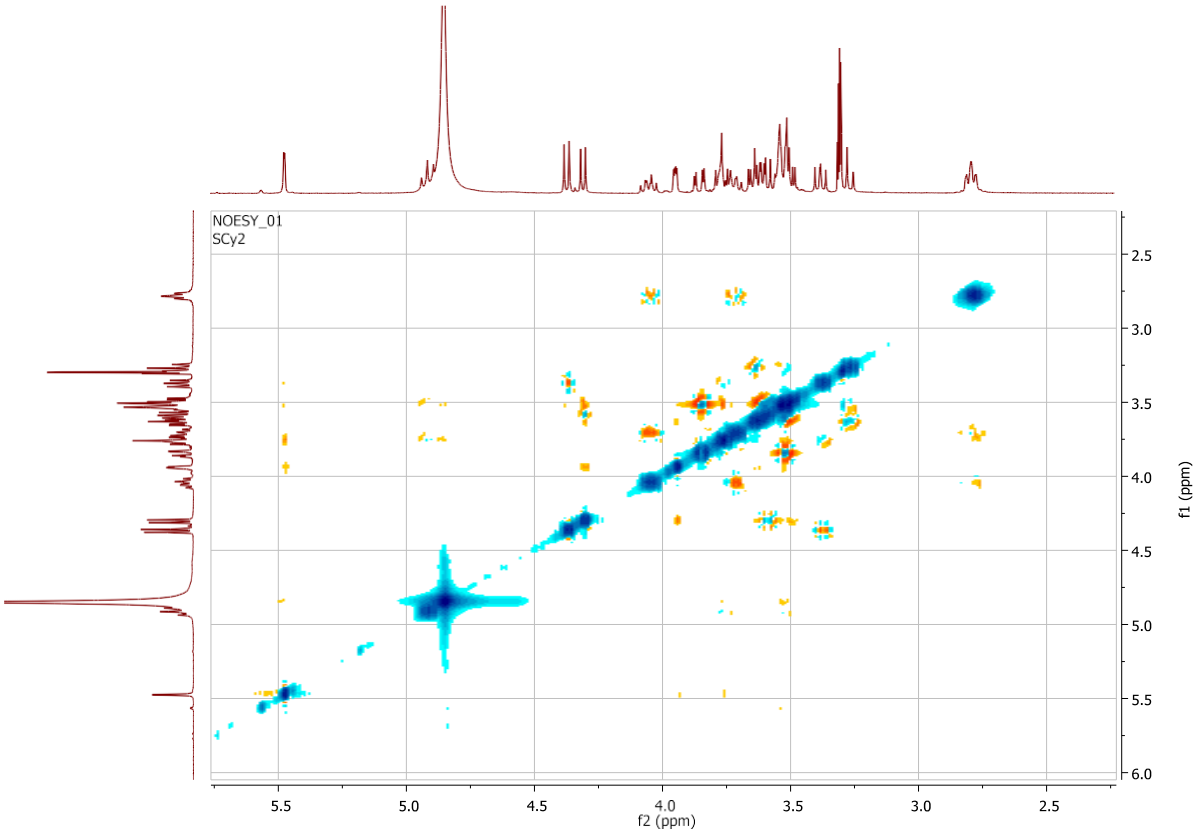


**Figure S26:** NOESY Spectrum of Compound **6** (Lavandulifolioside)

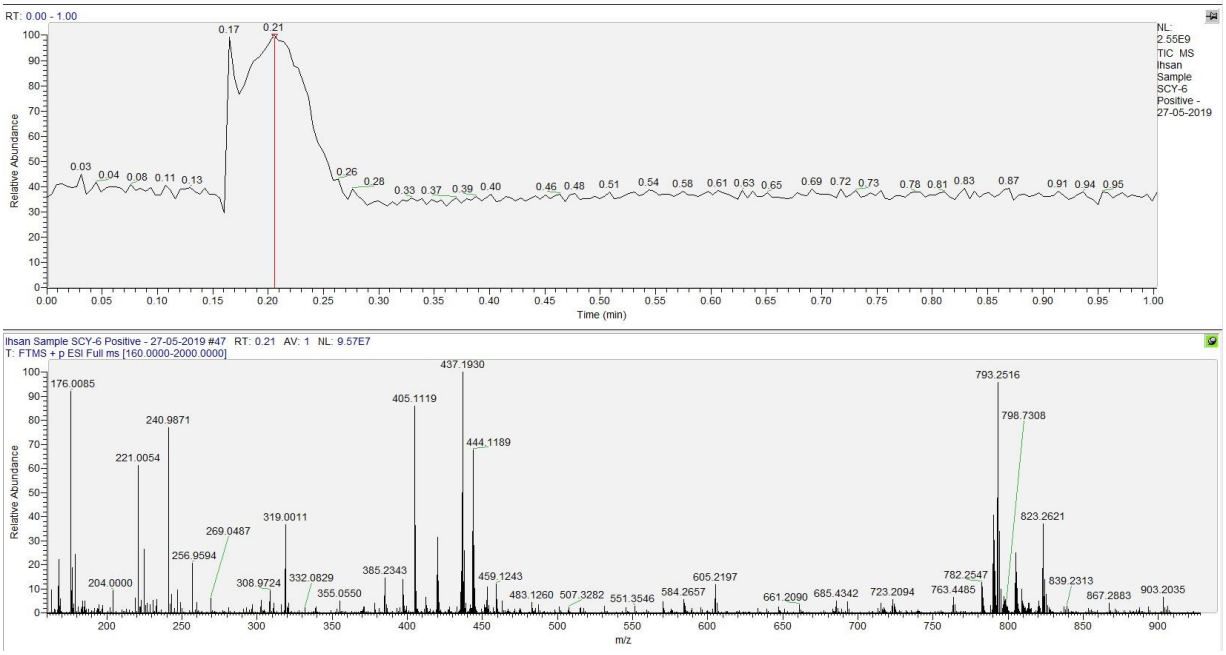


**Figure S27:** Positive- ion HRLCMS-MS Spectrum of Compound **7** (Leonoside A)

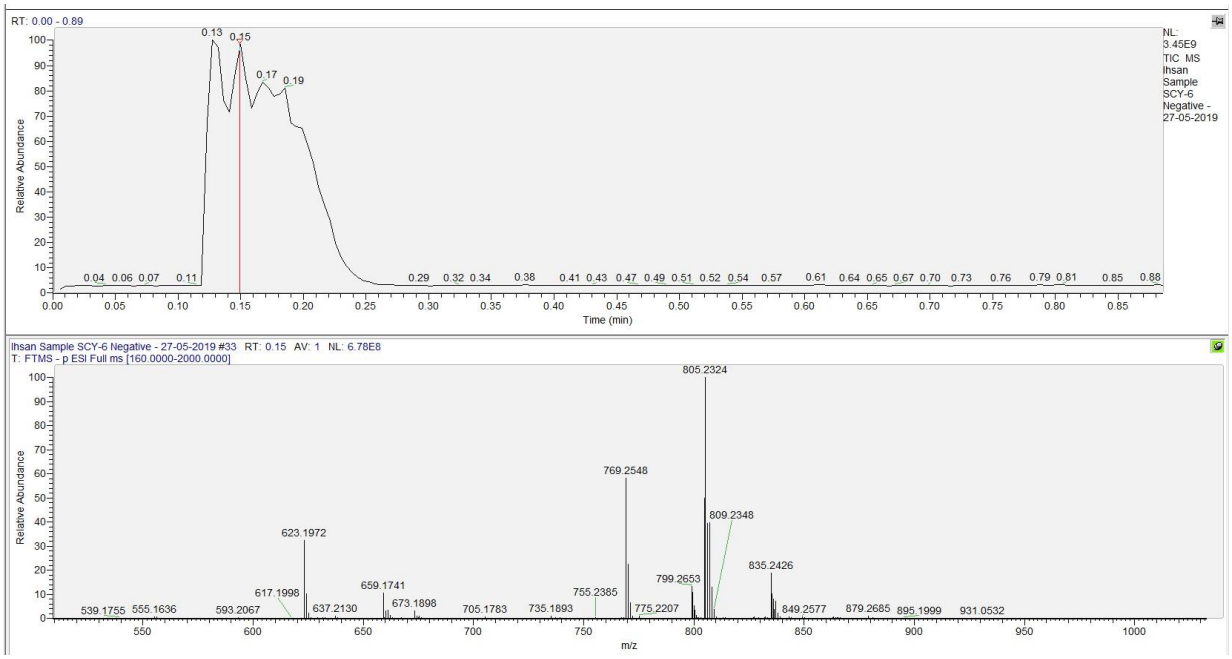


**Figure S28:** Negative- ion HRLCMS-MS Spectrum of Compound **7** (Leonoside A)

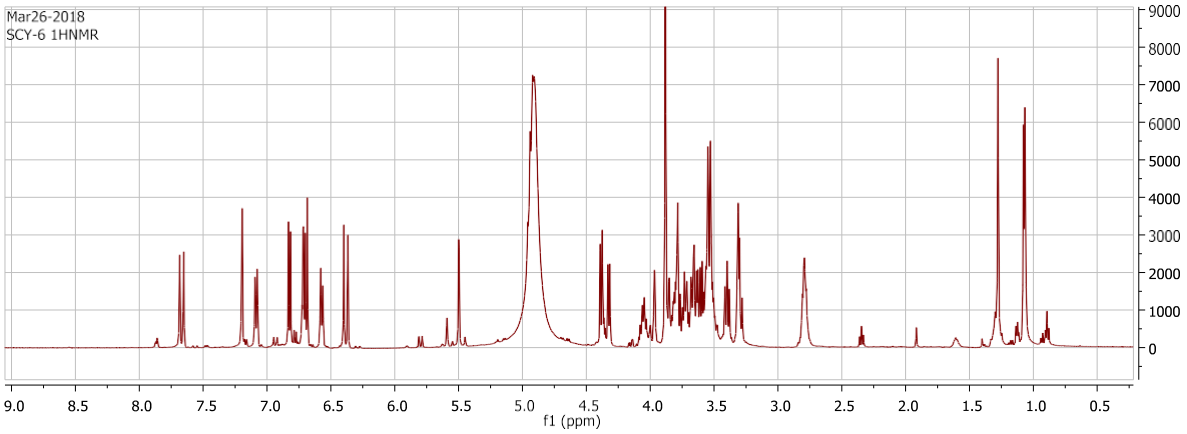


**Figure S29:** $^{1}$H-NMR (500 MHz, $CD_3OD$) Spectrum of Compound **7** (Leonoside A)

**Table 7:** The $^{1}H$ and $^{13}C$ NMR data of Compound **7** (Leonoside A) ($CD_3OD$; $\delta_H$ 500 MHz; $\delta_C$ 125 MHz)

| **C/H** | **DEPT** | **$\delta_C$** (ppm) | **$\delta_H$** (ppm), ***J*** (Hz) |
|---|---|---|---|
| Phenylethyl alcohol 1 | C | 131.4 | - |
| 2 | CH | 116.3 | 7.19 d (2.0) |
| 3 | C | 146.0 | - |
| 4 | C | 144.6 | - |
| 5 | CH | 117.1 | 6.82 d (8.0) |
| 6 | CH | 121.3 | 7.08 dd (8.0 / 2.0) |
| α | $CH_2$ | 72.2 | 4.05 ddd "dt" (7.0, 8.3)<br>3.72 ddd "dt" (7.0, 8.3) |
| β | $CH_2$ | 36.5 | 2.79 t (7.4) |
| Glucose 1' | CH | 104.1 | 4.38 d (8.0) |
| 2' | CH | 76.0 | 3.38 dd (7.9 / 9.0) |
| 3' | CH | 82.2 | 3.78 dd"t" (9.0) |
| 4' | CH | 70.3 | 4.94 dd"t" (9.0) |
| 5' | CH | 75.8 | 3.60 – 3.50† |
| 6' | $CH_2$ | 62.2 | 3.60 – 3.50† |
| Rhamnose 1" | CH | 101.9 | 5.50 d (1.7) |
| 2" | CH | 82.7 | 3.97dd (1.7, 3.4) |
| 3" | CH | 71.8 | 3.67 dd (3.4 / 9.5) |
| 4" | CH | 74.1 | 3.28 dd"t" (9.5) |
| 5" | CH | 70.4 | 3.60 – 3.50† |
| 6" | $CH_3$ | 18.4 | 1.08 d (6.2) |
| Arabinose 1"' | CH | 107.4 | 4.32 d (7.3) |
| 2"' | CH | 72.8 | 3.61 dd (7.3, 9.3) |
| 3"' | CH | 74.3 | 3.48-3.52† |
| 4"' | CH | 69.8 | 3.78† |
| 5"' | $CH_2$ | 67.3 | 3.84 dd (12.6, 2.6), 3. 60 – 3.50† |
| Ferulic acid1"" | C | 127.6 | - |
| 2"" | CH | 111.7 | 6.72 d (2.0) |
| 3"" | C | 149.3 | - |
| 4"" | C | 150.7 | - |
| 5"" | CH | 116.5 | 6.68d (8.2) |
| 6"" | CH | 124.3 | 6.57 dd (8.2 / 2.0) |
| α' | CH | 115.0 | 6.38 d (15.9) |
| β' | CH | 148.0 | 7.66 d (15.9) |
| C=O | C | 168.3 | - |
| $OCH_3$ | $CH_3$ | 56.4 | 3.88 s |

†) *J* values could not be determined due to overlap.

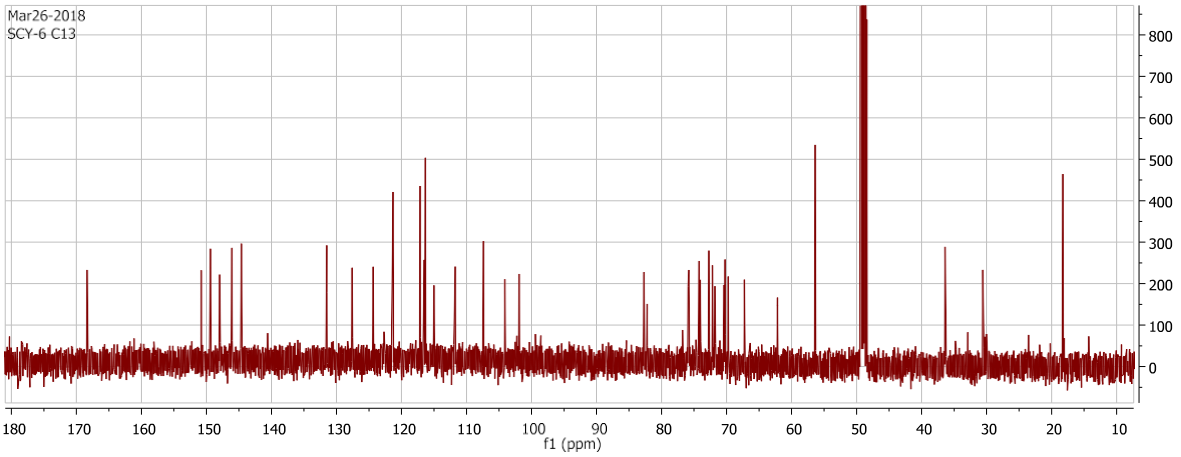


**Figure S30:** $^{13}$C-NMR (125 MHz, $CD_3OD$) Spectrum of Compound **7** (Leonoside A)

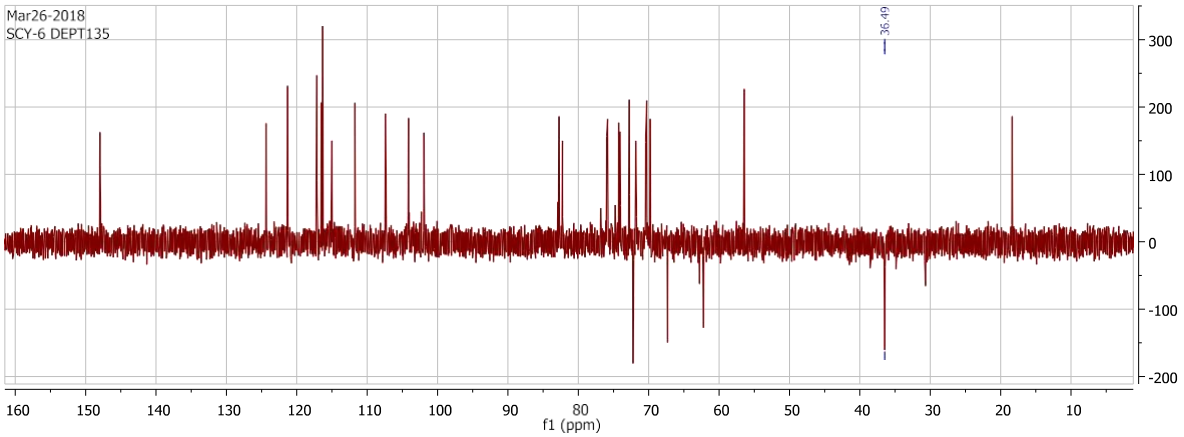


**Figure S31:** DEPT-135 Spectrum of Compound **7** (Leonoside A)

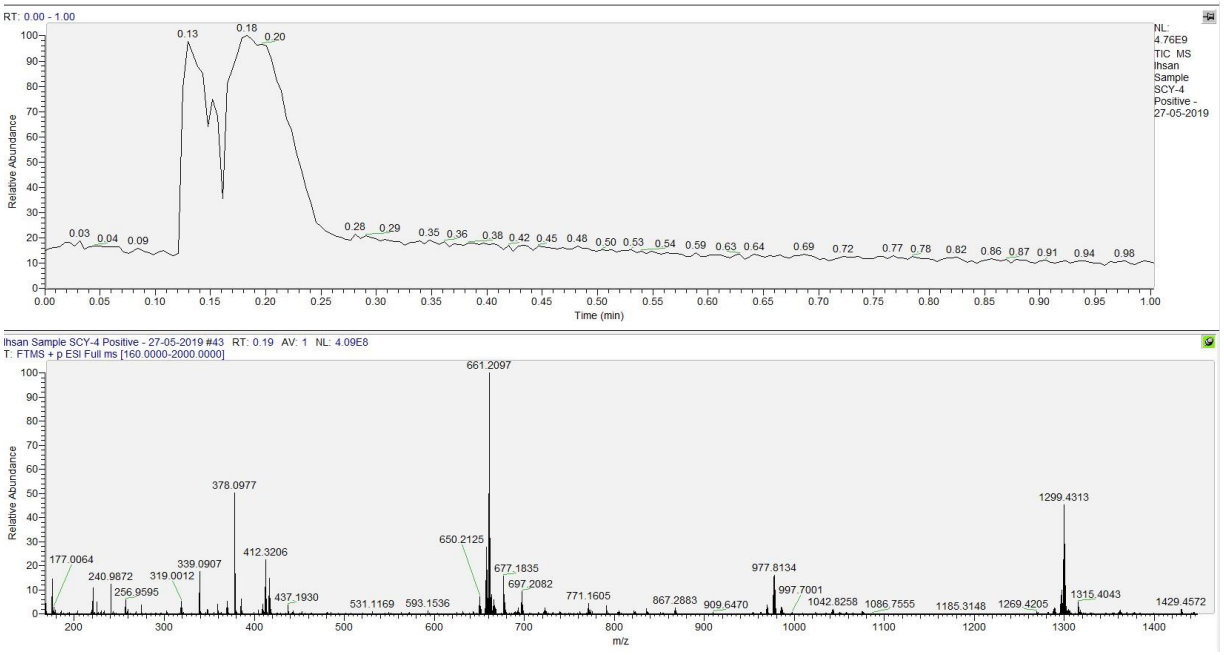


**Figure S32:** Positive- ion HRLCMS-MS Spectrum of Compound **8** (Leucoseptoside A)

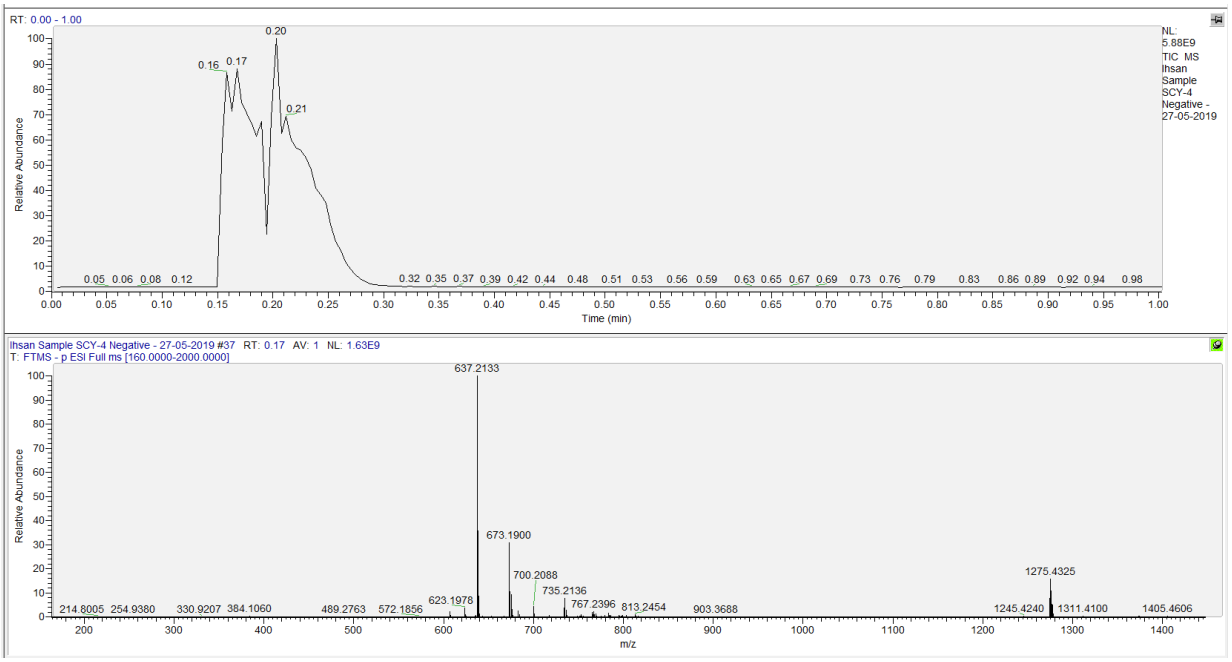


**Figure 33:** Negative- ion HRLCMS-MS Spectrum of Compound **8** (Leucoseptoside A)

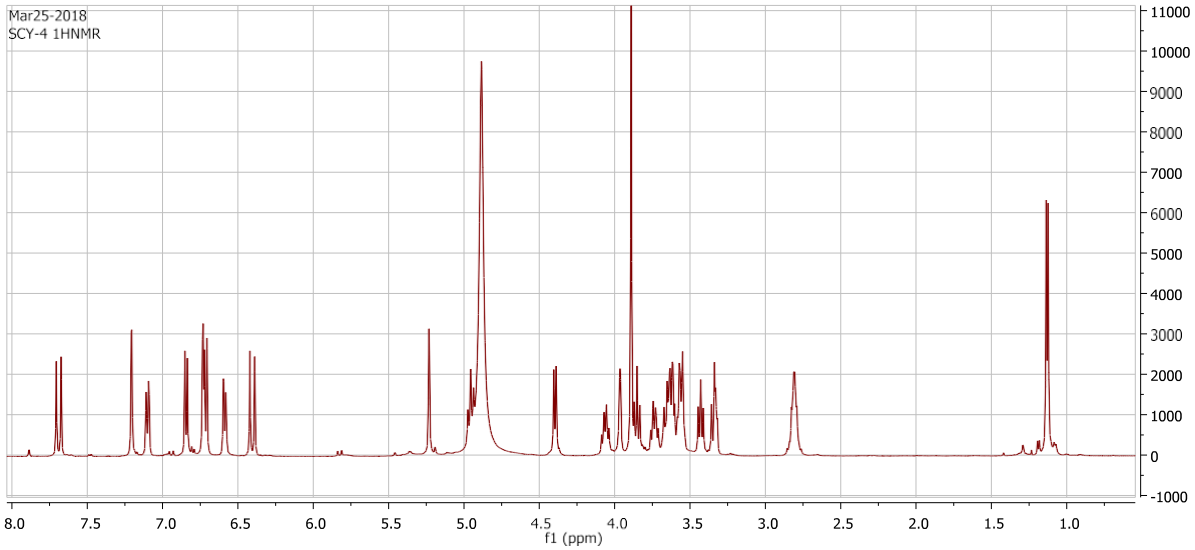


**Figure S34:** $^{1}$H-NMR (500 MHz, $CD_3OD$) Spectrum of Compound **8** (Leucoseptoside A)

**Table 8:** The $^{1}H$ and $^{13}C$ NMR data of Compound **8** (Leucoseptoside A) ($CD_3OD$; $\delta_H$ 500 MHz; $\delta_C$ 125 MHz)

| **C/H** | **DEPT** | **$\delta_C$** (ppm) | **$\delta_H$** (ppm), ***J*** (Hz) |
|---|---|---|---|
| Fenylethyl alcohol 1 | C | 131.4 | - |
| 2 | CH | 117.1 | 6.73 d (1.8) |
| 3 | C | 146.0 | - |
| 4 | C | 144.5 | - |
| 5 | CH | 116.4 | 6.71 d (8.1) |
| 6 | CH | 121.3 | 6.59 dd (8.1 / 1.8) |
| α | $CH_2$ | 72.0 | 4.06 ddd "dt" (7.0, 8.3)<br>3.73 ddd "dt" (7.0, 8.3) |
| β | $CH_2$ | 36.4 | 2.81 ddd (7.0, 8.3) |
| Glucose 1' | CH | 104.1 | 4.39 d (8.0) |
| 2' | CH | 76.1 | 3.43 dd (8.0/ 9.0) |
| 3' | CH | 81.4 | 3.85 dd"t" (9.0) |
| 4' | CH | 70.5 | 4.95 dd"t" (9.0) |
| 5' | CH | 75.8 | 3.53† |
| 6' | $CH_2$ | 62.1 | 3.62†, 3.52† |
| Rhamnose 1" | CH | 102.9 | 5.23 d (1.7) |
| 2" | CH | 72.2 | 3.96 dd (1.7, 3.2) |
| 3" | CH | 71.9 | 3.58 dd (3.2, 9.6) |
| 4" | CH | 73.7 | 3.34 dd"t" (9.6) |
| 5" | CH | 70.3 | 3.55† |
| 6" | $CH_3$ | 18.4 | 1.13 d (6.2 |
| Ferulic acid 1"' | C | 127.6 | - |
| 2"' | CH | 111.7 | 7.20 d (1.8) |
| 3"' | C | 149.3 | - |
| 4"' | C | 150.6 | - |
| 5"' | CH | 116.5 | 6.84 d (8.2) |
| 6"' | CH | 124.3 | 7.10 dd (8.2 / 1.8) |
| α' | CH | 115.0 | 6.40 d (16.0) |
| β' | CH | 147.9 | 7.69 d (16.0) |
| C=O | C | 168.3 | - |
| OMe | $CH_3$ | 56.4 | 3.89 s |

†) *J* values could not be determined due to overlap.

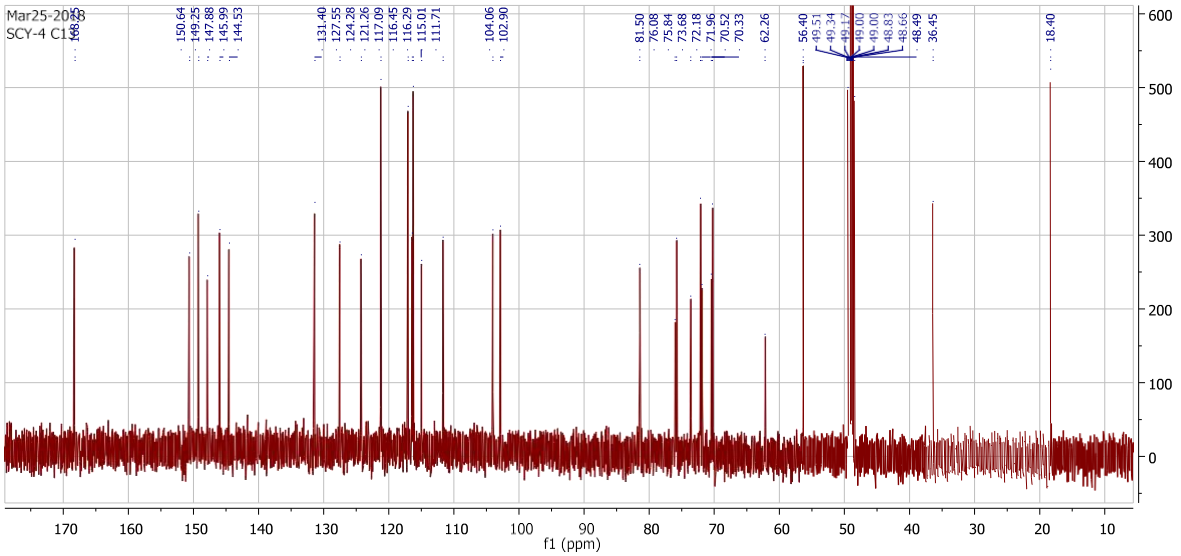


**Figure S35:** $^{13}$C-NMR (125 MHz, $CD_3OD$) Spectrum of Compound **8** (Leucoseptoside A)

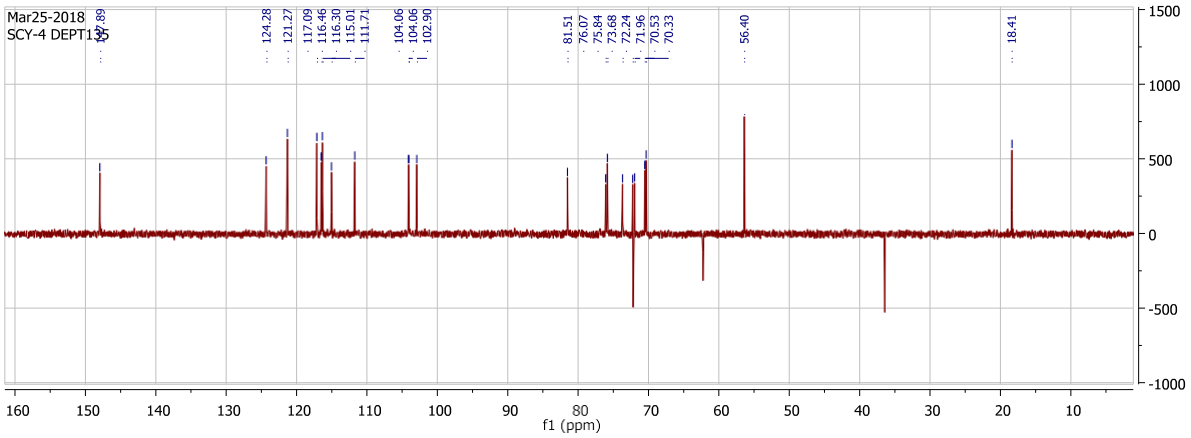


**Figure S36:** DEPT-135 Spectrum of Compound **8** (Leucoseptoside A)

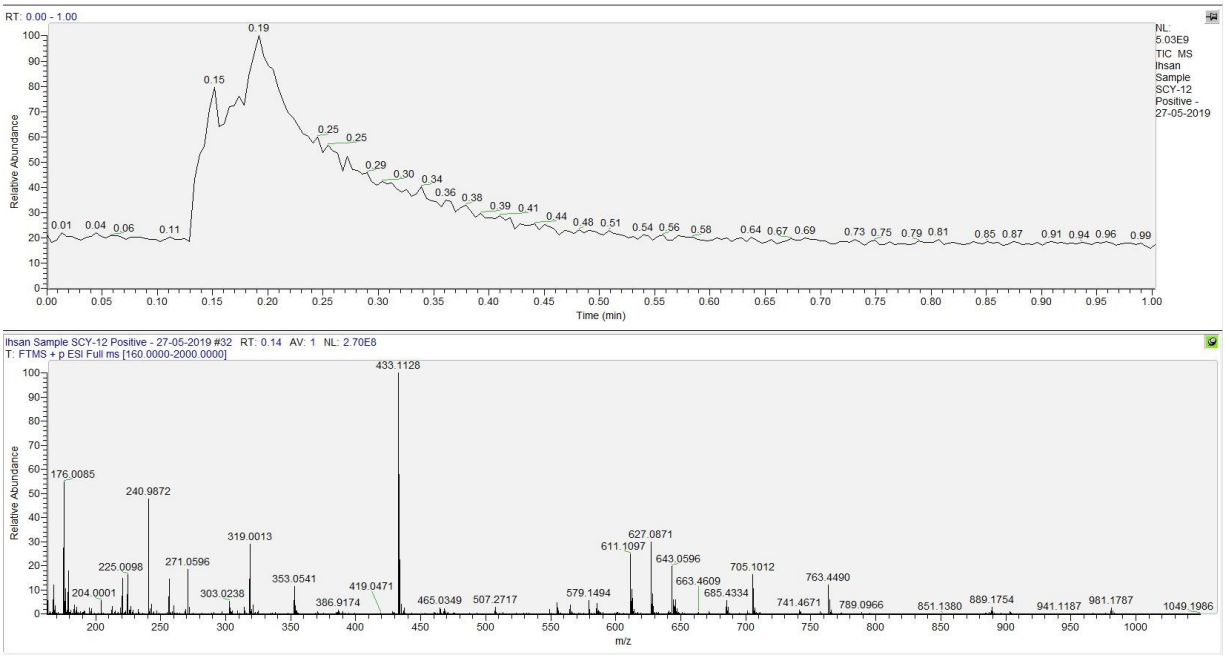


**Figure S37:** Positive- ion HRLCMS-MS Spectrum of Compound **9** (Apigenin 7-*O*-glucopyranoside)

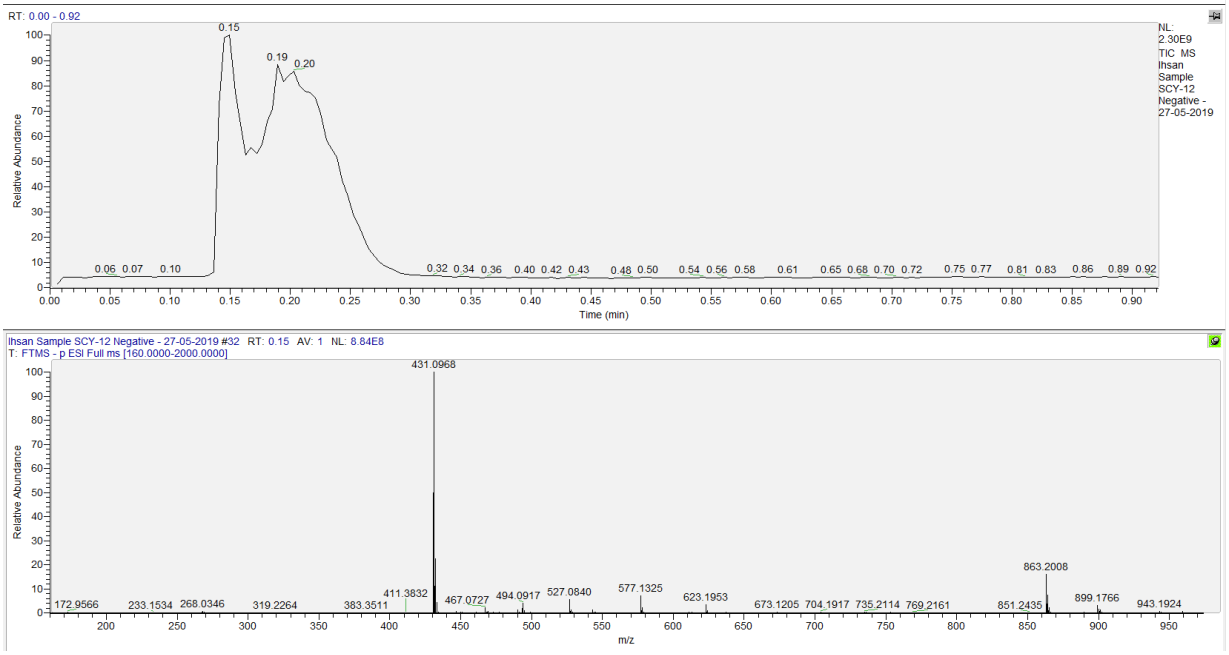


**Figure S38:** Negative- ion HRLCMS-MS Spectrum of Compound **9** (Apigenin 7-*O*-glucopyranoside)

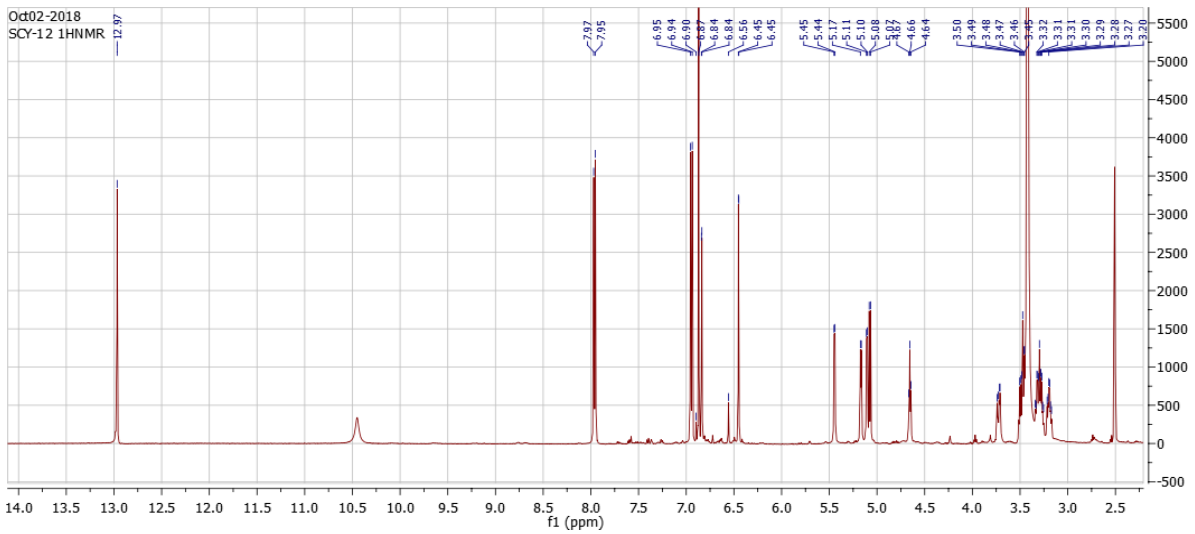


**Figure S39:** $^{1}$H-NMR (500 MHz, DMSO-$d_6$) Spectrum of Compound **9** (Apigenin 7-*O*-glucopyranoside)

**Table 9:** The $^{1}H$ and $^{13}C$ NMR data of Compound **9** (Apigenin 7-*O*-glucopyranoside) (DMSO-$d_6$; $\delta_H$ 500 MHz; $\delta_C$ 125 MHz)

| **C/H** | **DEPT** | **$\delta_C$** (ppm) | **$\delta_H$** (ppm), ***J*** (Hz) |
|---|---|---|---|
| Apigenin 2 | C | 164.7 | - |
| 3 | CH | 103.6 | 6.87 s |
| 4 | C | 182.5 | - |
| 5 | C | 161.8 | - |
| 6 | CH | 99.9 | 6.45 d (1.8) |
| 7 | C | 163.4 | - |
| 8 | CH | 95.3 | 6.84 d (1.8) |
| 9 | C | 157.4 | - |
| 10 | C | 105.8 | - |
| 1' | C | 121.5 | - |
| 2' | CH | 129.1 | 7.96 d (8.9) |
| 3' | CH | 116.5 | 6.95 d (8.9) |
| 4′ | C | 161.6 | - |
| 5′ | CH | 116.5 | 6.95 d (8.9) |
| 6' | CH | 119.6 | 7.96 d (8.9) |
| 5-OH | - | - | 13.0 s |
| Glucose 1" | CH | 100.4 | 5.07 d (7.5) |
| 2" | CH | 73.4 | 3.28 m |
| 3" | CH | 76.9 | 3.30 m |
| 4" | CH | 70.1 | 3.19 m |
| 5" | CH | 77.6 | 3.45 m |
| 6" | $CH_2$ | 61.1 | 3.72 m, 3.48 m |
| 2"-OH | - | - | 5.45 d (5.0) |
| 3"-OH | - | - | 5.11 d (5.3) |
| 4"-OH | - | - | 5.17 d (5.0) |
| 6"-OH | - | - | 4.66 t (5.9) |

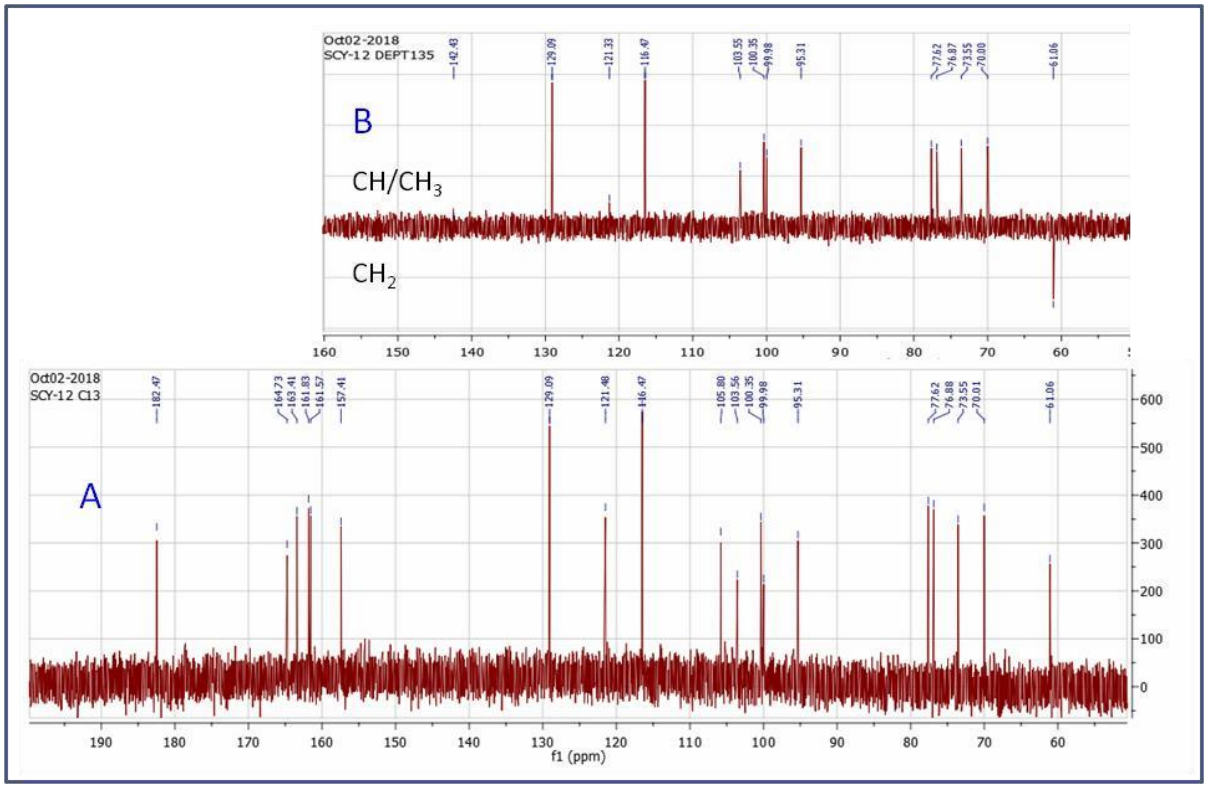


**Figure S40:** $^{13}$C-NMR (A) + DEPT-135 (B) (125 MHz, DMSO-$d_6$) Spectrum of Compound **9** (Apigenin 7-*O*-glucopyranoside)

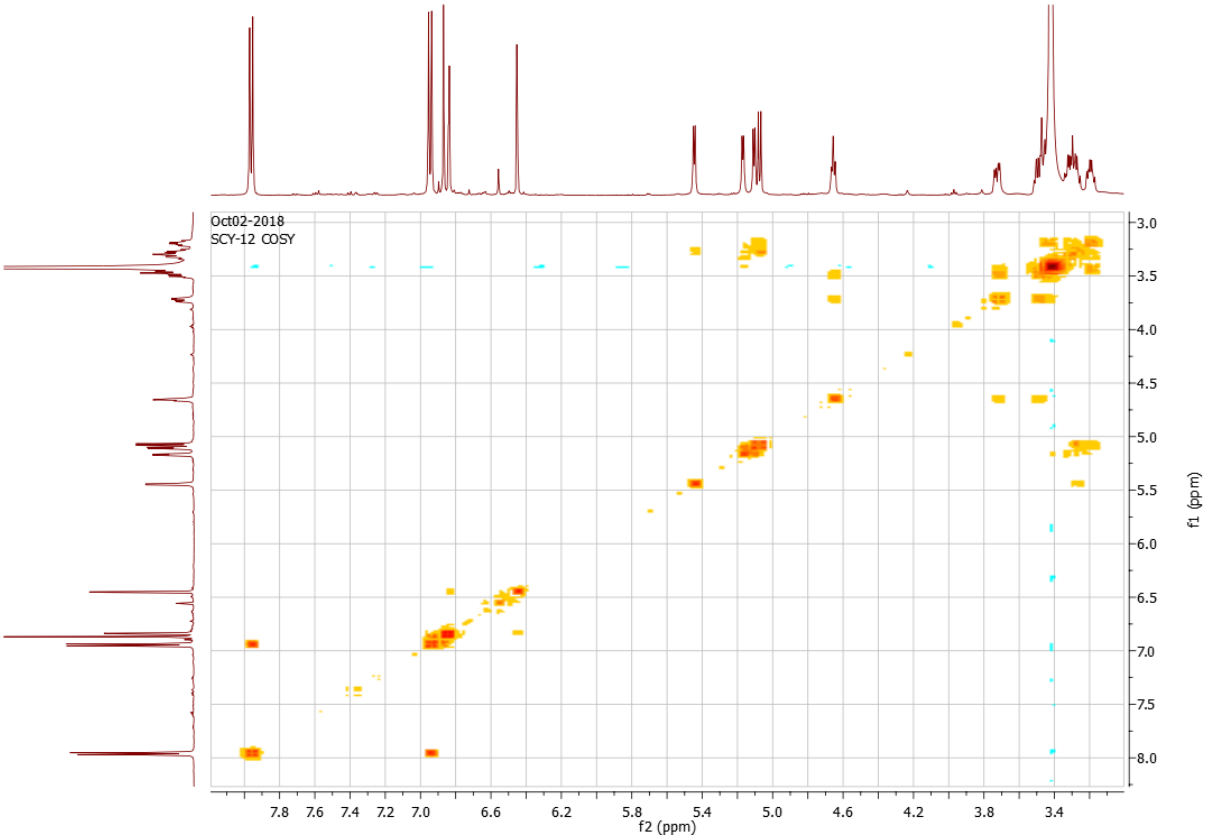


**Figure S41:** COSY Spectrum of Compound **9** (Apigenin 7-*O*-glucopyranoside)

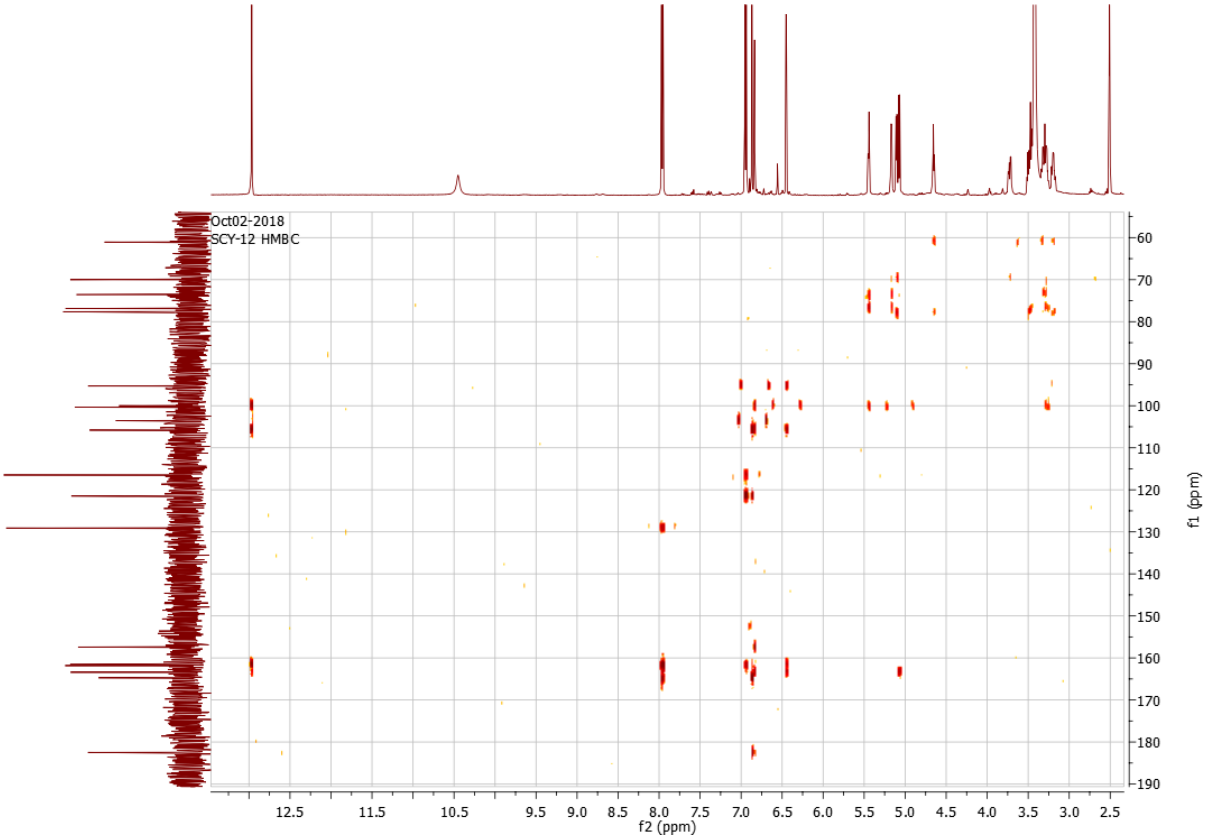


**Figure S42:** HMBC Spectrum of Compound **9** (Apigenin 7-*O*- glucopyranoside)

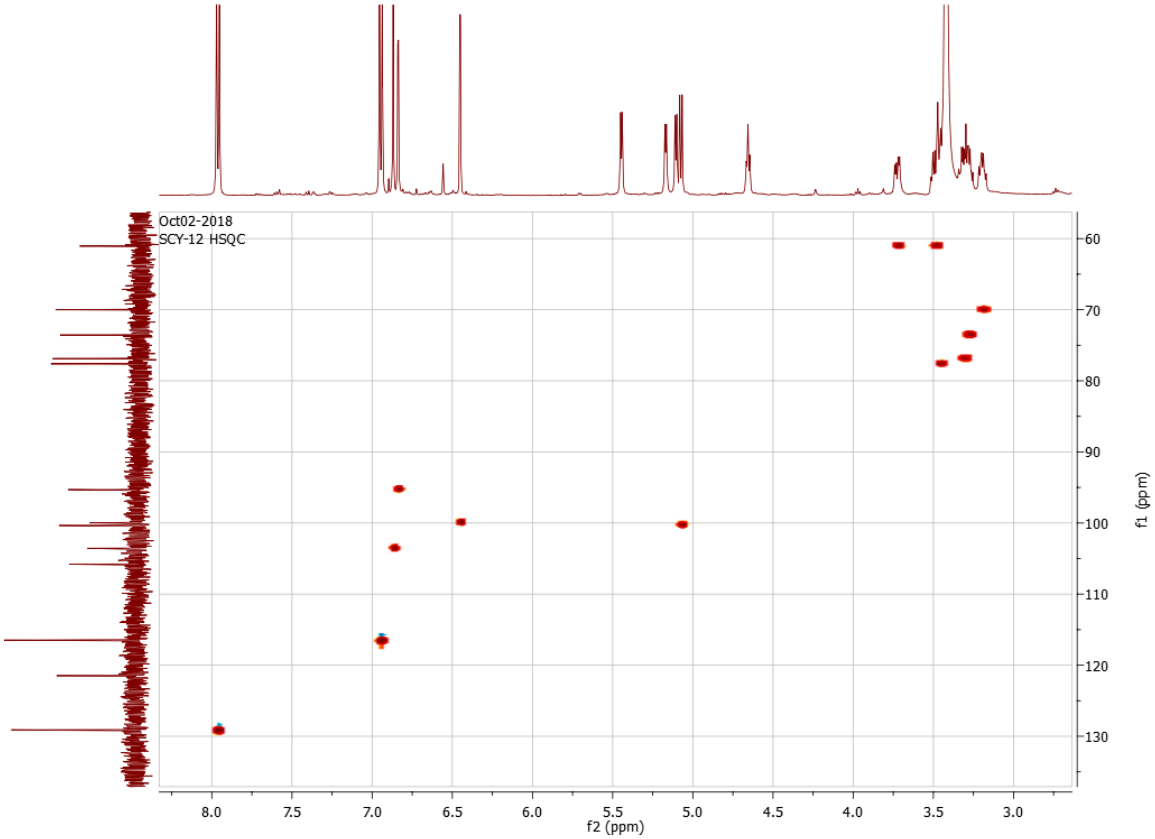


**Figure S43:** HSQC Spectrum of Compound **9** (Apigenin 7-*O*-glucopyranoside)

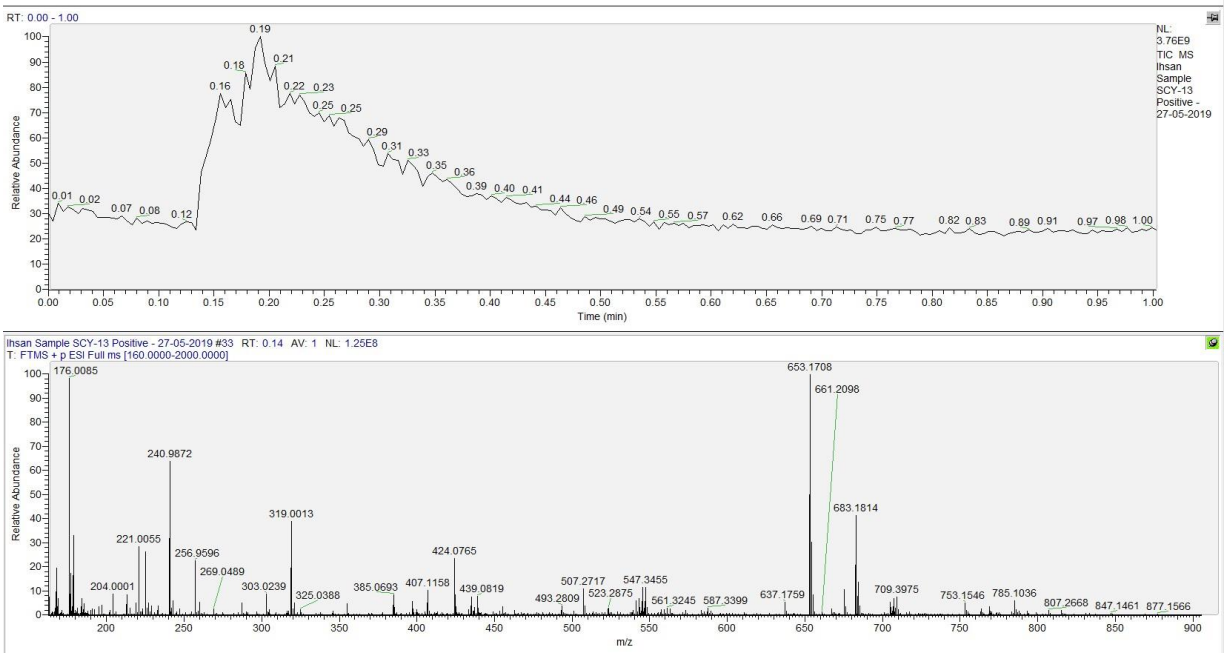


**Figure S44:** Positive- ion HRLCMS-MS Spectrum of Compound **10** (Isoscutellarein-7-*O*-[6'''-*O*-acetyl-allopyranosyl-(1→2)-glucopyranoside])

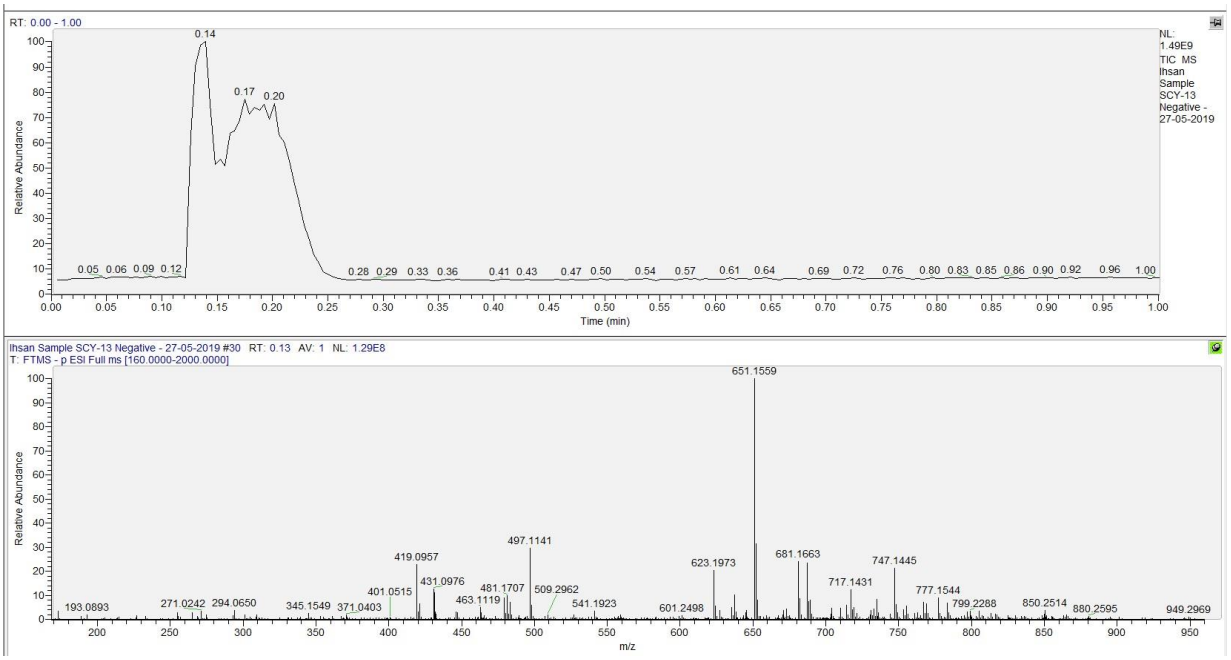


**Figure S45:** Negative- ion HRLCMS-MS Spectrum of Compound **10** (Isoscutellarein-7-*O*-[6'''-*O*-acetyl-allopyranosyl- (1→2)-glucopyranoside])

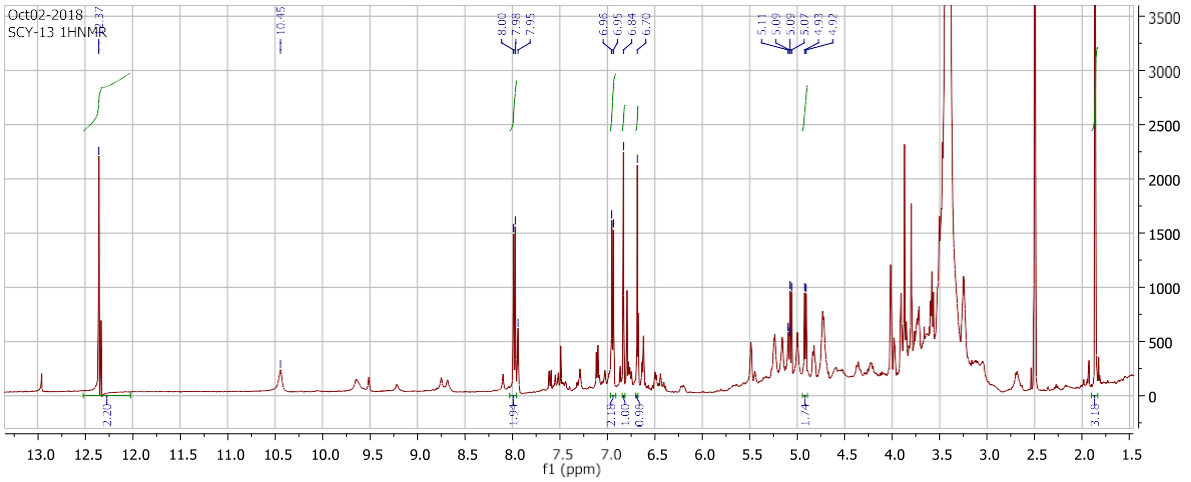


**Figure S46:** $^{1}$H-NMR (500 MHz, DMSO-$d_6$) Spectrum of Compound **10** (Isoscutellarein-7-*O*-[6'''-*O*-acetyl-allopyranosyl-(1→2)-glucopyranoside])

**Table 9:** The $^{1}H$ and $^{13}C$ NMR data of Compound **10** (Isoscutellarein-7-*O*-[6'''-*O*-acetyl-allopyranosyl-(1→2)-glucopyranoside]) (DMSO-$d_6$; $\delta_H$ 500 MHz; $\delta_C$ 125 MHz)

| **C/H** | **DEPT** | **$\delta_C$** (ppm) | **$\delta_H$** (ppm), ***J*** (Hz) |
|---|---|---|---|
| Isoscutellarein 2 | C | 164.5 | - |
| 3 | CH | 99.8 | 6.84 s |
| 4 | C | 182.7 | - |
| 5 | C | 152.0 | - |
| 6 | CH | 103.1 | 6.70 s |
| 7 | C | 151.0 | - |
| 8 | C | 128.0 | - |
| 9 | C | 144.0 | - |
| 10 | C | 100.0 | - |
| 1' | C | 121.6 | - |
| 2' | CH | 129.1 | 7.99 d (8.8) |
| 3' | CH | 116.5 | 6.96 d (8.8) |
| 4′ | C | 161.7 | - |
| 5′ | CH | 116.5 | 6.96 d (8.8) |
| 6' | CH | 129.1 | 7.99 d (8.8) |
| 5-OH | - | - | 12.37 s |
| Glucose 1'' | CH | 100.5 | 5.08 d |
| 2'' | CH | 83.0 | 3.59 dd |
| 3'' | CH | 76.1 | 3.52 † |
| 4'' | CH | 69.6 | 3.25 † |
| 5'' | CH | 77.5 | 3.46 † |
| 6'' | $CH_2$ | 61.0 | 3.74, 3.50 † |
| Allose 1''' | CH | 102.9 | 4.92 d |
| 2''' | CH | 71.9 | 3.25 † |
| 3''' | CH | 71.3 | 3.91 † |
| 4''' | CH | 67.0 | 3.42 † |
| 5''' | CH | 71.9 | 3.86 † |
| 6''' | $CH_2$ | 63.0 | 4.01 † |
| $\underline{C}OCH_3$ | C | 171.8 | - |
| $CO\underline{C}H_3$ | $CH_3$ | 21.1 | 1.87 s |

†) *J* values could not be determined due to overlap.

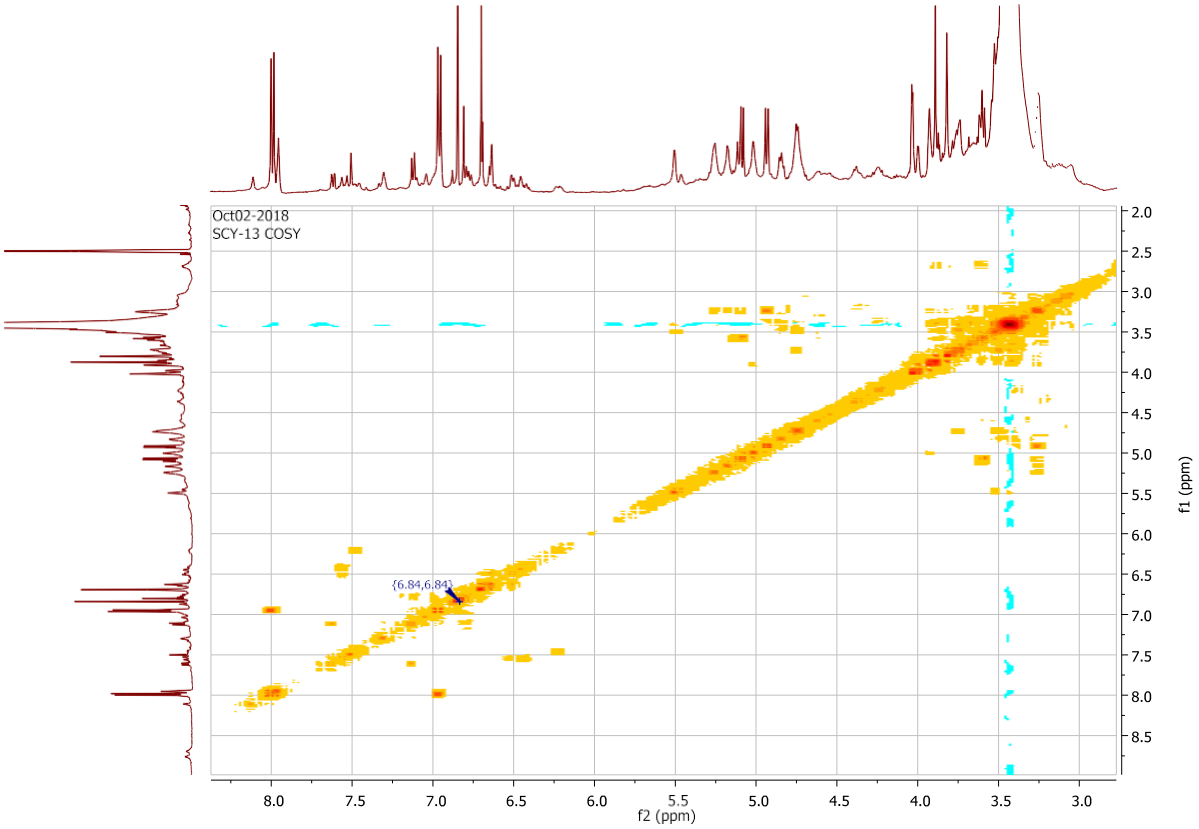


**Figure S47:** COSY Spectrum of Compound **10** (Isoscutellarein-7-*O*-[6'''-*O*-acetyl-allopyranosyl-(1→2)-glucopyranoside])

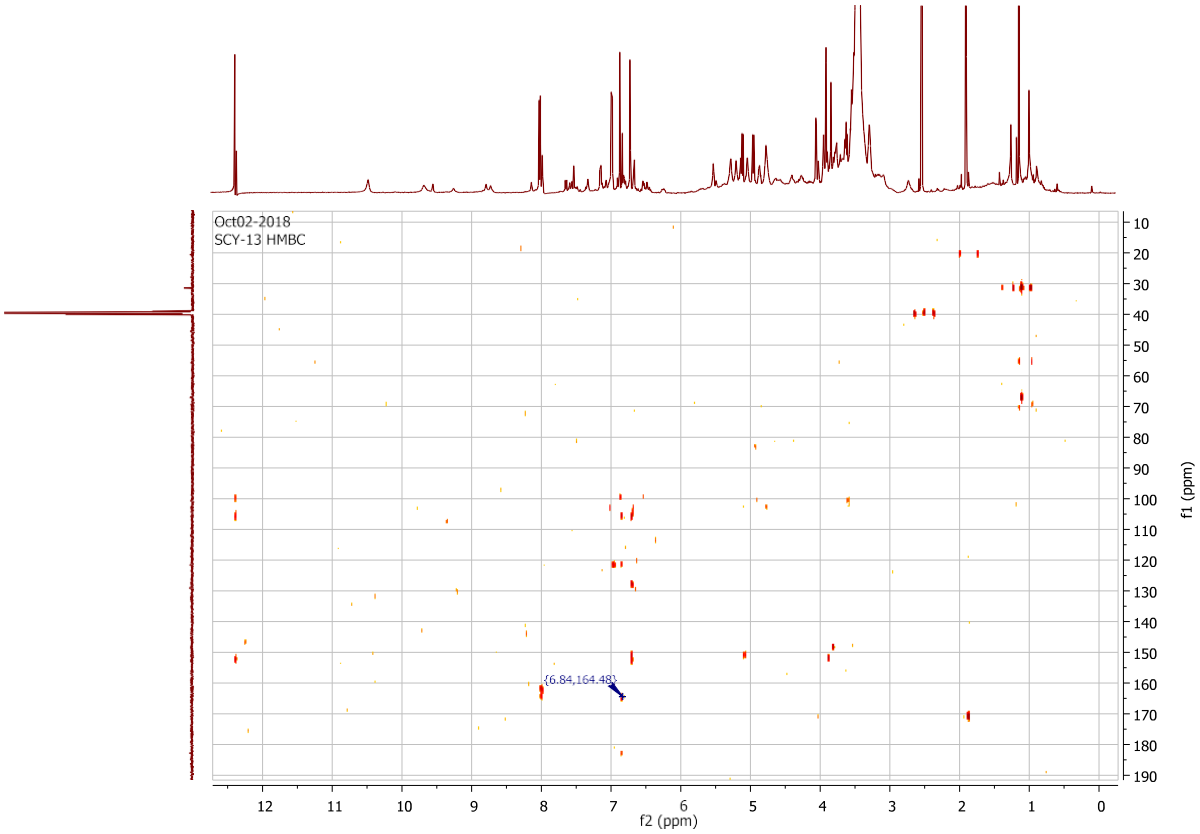


**Figure S48:** HMBC Spectrum of Compound **10** (Isoscutellarein-7-*O*-[6'''-*O*-acetyl-allopyranosyl-(1→2)-glucopyranoside])

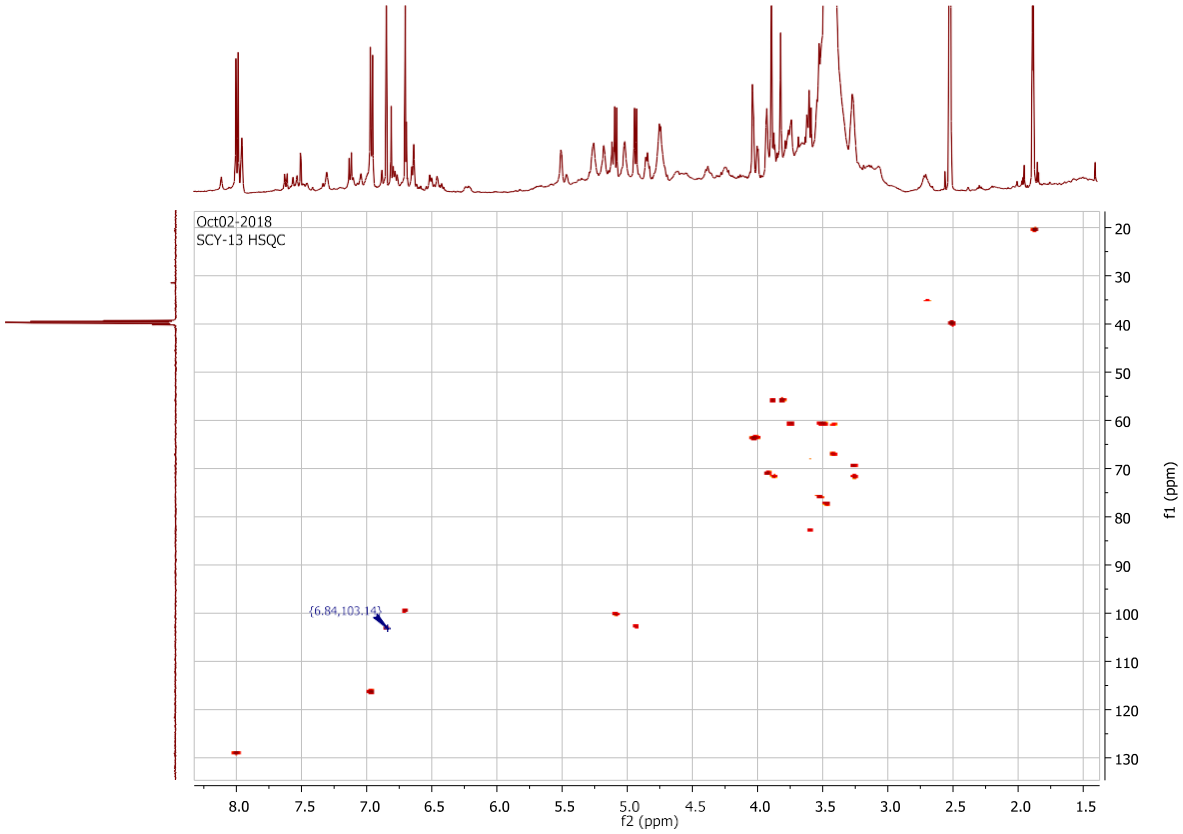


**Figure S49:** HSQC Spectrum of Compound **10** (Isoscutellarein-7-*O*-[6'''-*O*-acetyl-allopyranosyl-(1→2)-glucopyranoside])

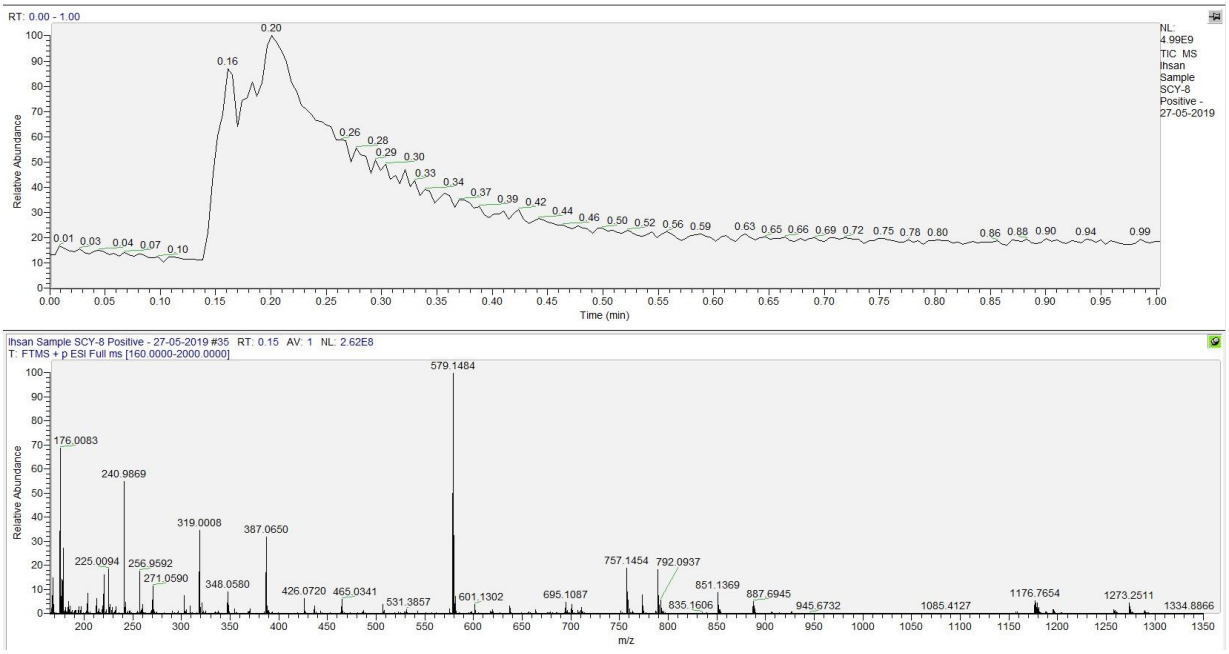


**Figure S50:** Positive- ion HRLCMS-MS Spectrum of Compound **11 & 12** (Apigenin 7-*O*-(4"-*O*-*p*-coumaryl)-glucopyranoside & Apigenin 7-*O*-(3"-*O*-*p*-coumaroyl)-glucopyranoside)

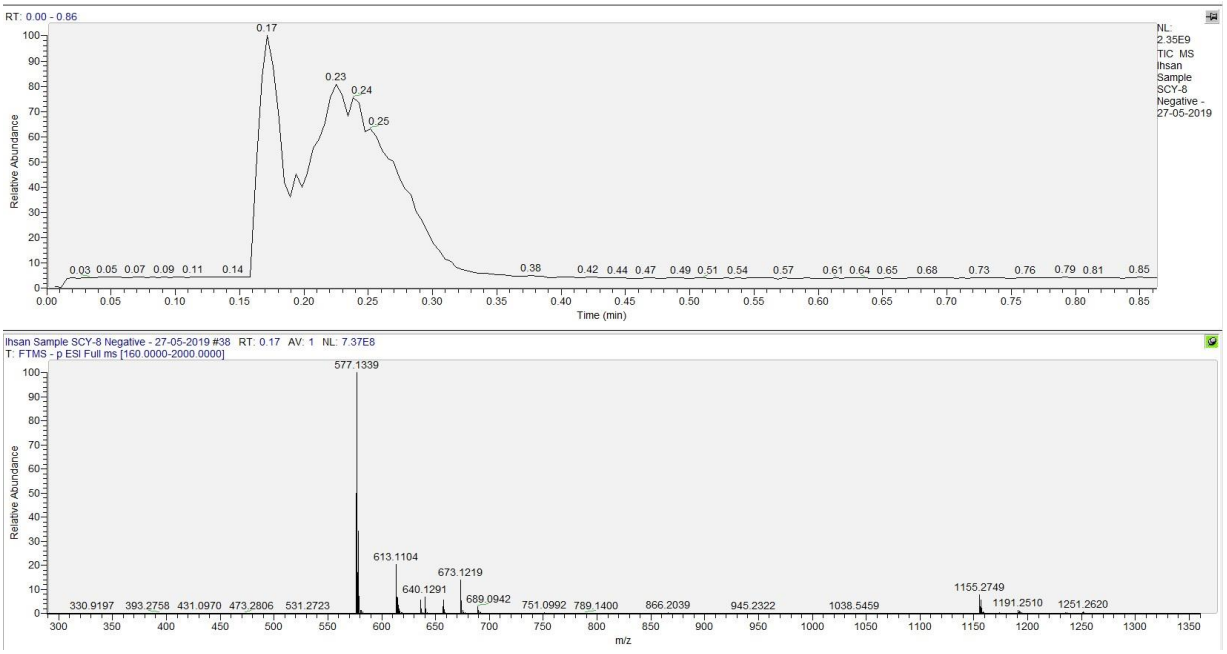


**Figure S51:** Negative- ion HRLCMS-MS Spectrum of Compound **11 & 12** (Apigenin 7-*O*-(4''-*O*-*p*-coumaryl)-glucopyranoside & Apigenin 7-*O*-(3''-*O*-*p*-coumaroyl)-glucopyranoside)

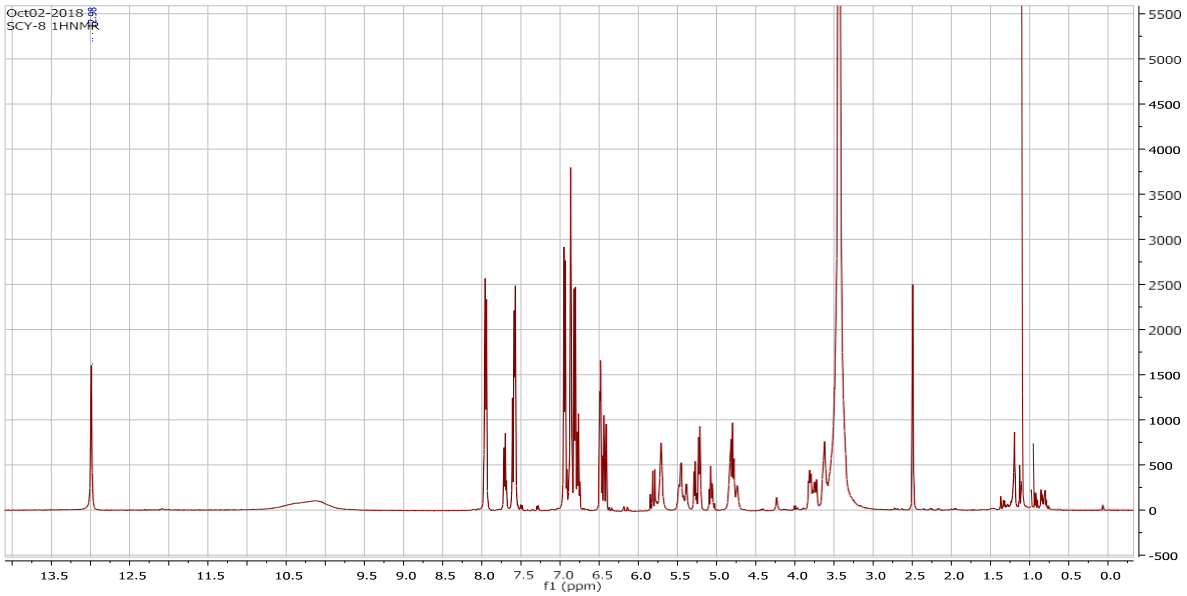


**Figure S52:** $^{1}$H-NMR (500 MHz, DMSO-$d_6$) Spectrum of Compound **11 & 12** (Apigenin 7-*O*-(4"-*O*-*p*-coumaryl)- glucopyranoside & Apigenin 7-*O*-(3"-*O*-*p*-coumaroyl)-glucopyranoside)

**Table 10:** The $^{1}H$ and $^{13}C$ NMR data of Compound **11&12** (Apigenin 7-*O*-(4"-*O*-*p*-coumaryl)-glucopyranoside & Apigenin 7-*O*-(3"-*O*-*p*-coumaroyl)-glucopyranoside) (DMSO-$d_6$; $\delta_H$ 500 MHz; $\delta_C$ 125 MHz)

| | | **11** | | **12** | |
|---|---|---|---|---|---|
| **C/H** | **DEPT** | **$\delta_C$** (ppm) | **$\delta_H$** (ppm), ***J*** (Hz) | **$\delta_C$** (ppm) | **$\delta_H$** (ppm), ***J*** (Hz) |
| Apigenin 2 | C | 164.7 | - | | |
| 3 | CH | 103.6 | 6.86 s | | |
| 4 | C | 182.5 | - | | |
| 5 | C | 161.8 | - | | |
| 6 | CH | 99.8 | 6.48 d (1.8) | | |
| 7 | C | 163.4 | - | | |
| 8 | CH | 95.4 | 6.86 d (1.8) | | |
| 9 | C | 157.4 | - | | |
| 10 | C | 105.8 | - | | |
| 1' | C | 121.5 | - | | |
| 2' | CH | 129.1 | 7.95 d (8.5) | | |
| 3' | CH | 116.5 | 6.94 d (8.5) | | |
| 4′ | C | 161.6 | - | | |
| 5′ | CH | 116.5 | 6.94 d (8.5) | | |
| 6' | CH | 129.1 | 7.95 d (8.5) | | |
| 5-OH | - | - | 13.0 s | | |
| Glucose 1" | CH | 100.4 | 5.22 d (7.6) | 100.4 | 5.28 d (7.6) |
| 2" | CH | 73.7 | 3.39 m | 71.6 | 3.51 m |
| 3" | CH | 74.3 | 3.62 m | 77.7 | 5.07 dd "t" (9.5) |
| 4" | CH | 71.2 | 4.80 dd “t” (9.5) | 67.9 | 3.48† |
| 5" | CH | 75.3 | 3.81 m | 77.3 | 3.63† |
| 6" | $CH_2$ | 60.9 | 3.49 †, 3.38 † | 60.9 | 3.74†, 3.54† |
| *p*- coumaryl 1'" | C | 125.5 | - | 125.6 | - |
| 2'"/6'" | CH | 130.9 | 7.58 d (8.2) | 130.6 | 7.60 d (8.2) |
| 3'"/5'" | CH | 116.3 | 6.81 d (8.2) | 116.6 | 6.81 d (8.2) |
| 4'" | C | 160.2 | - | 160.2 | - |
| α | CH | 114.6 | 6.42 d (16.0) | 115.4 | 6.44 d (16.0) |
| β | CH | 145.5 | 7.59 d (16.0) | 145.0 | 7.60 d (16.0) |
| C=O | C | 166.4 | - | 166.7 | - |

†) *J* values could not be determined due to overlap.

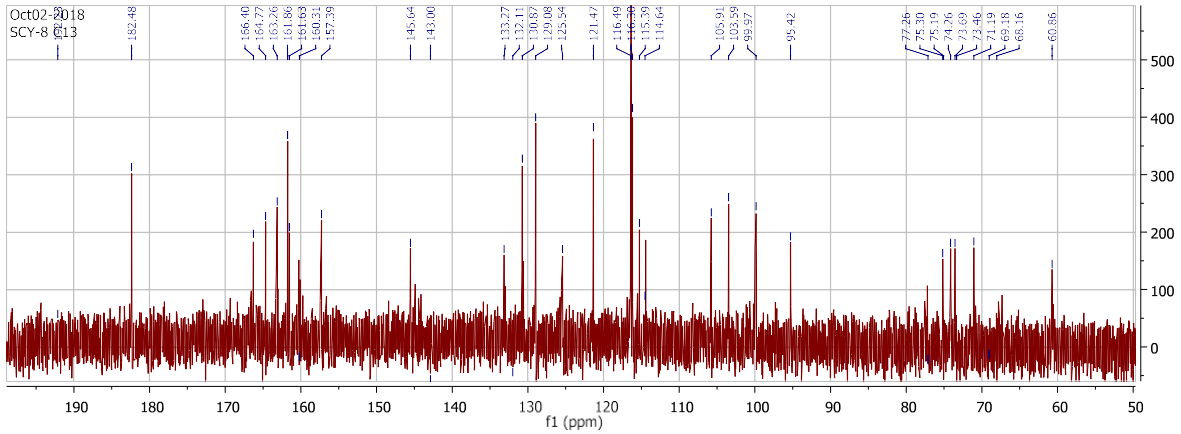


**Figure S53:** $^{13}$C-NMR (125 MHz, DMSO-$d_6$) Spectrum of Compound **11 & 12** (Apigenin 7- *O*-(4"-*O*-*p*-coumaryl)- glucopyranoside & Apigenin 7-*O*-(3"-*O*-*p*-coumaroyl)-glucopyranoside)

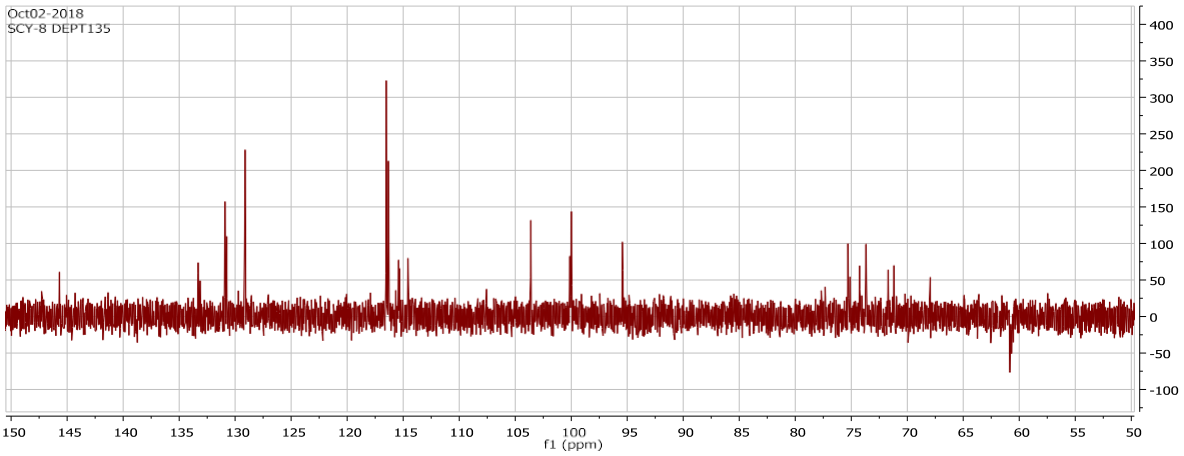


**Figure S54:** DEPT-135 Spectrum of Compound **11 & 12** (Apigenin 7-*O*-(4"-*O*-*p*-coumaryl)-glucopyranoside & Apigenin 7-*O*-(3"-*O*-*p*-coumaroyl)-glucopyranoside)

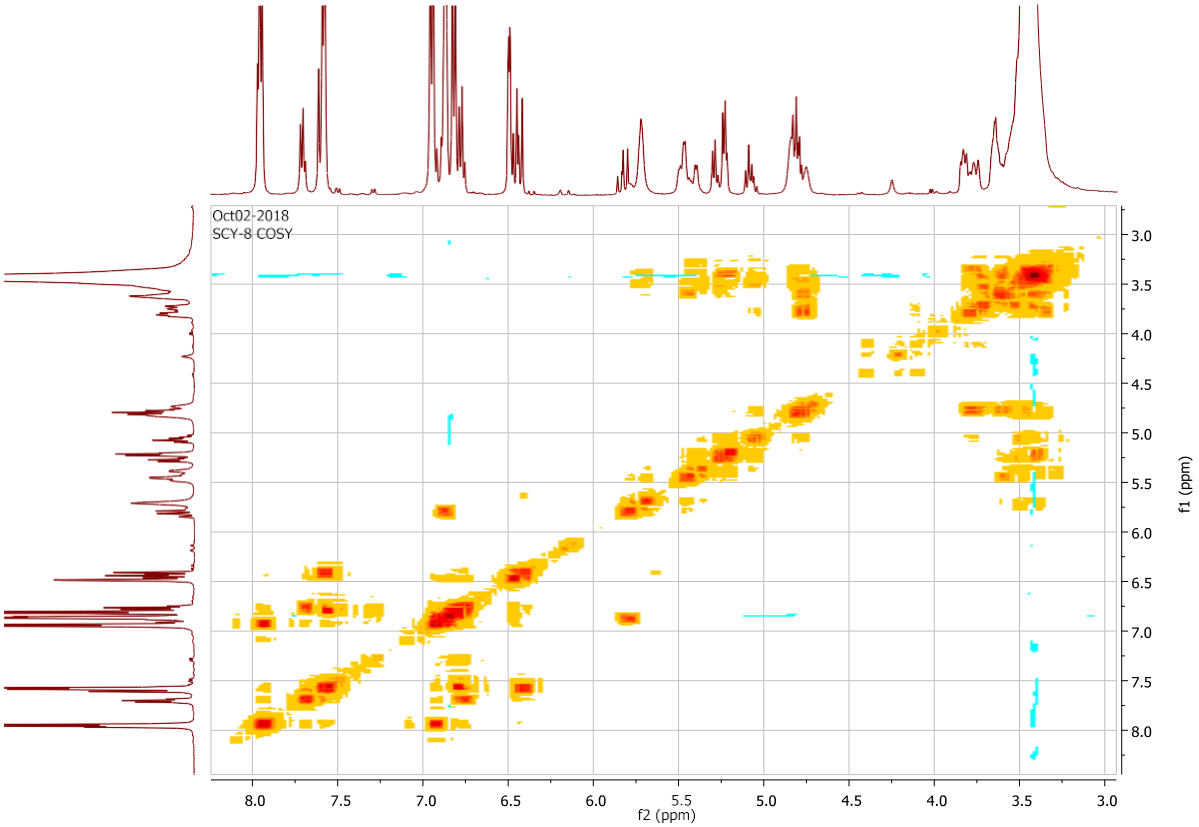


**Figure S55:** COSY Spectrum of Compound **11 & 12** (Apigenin 7-*O*-(4"-*O*-*p*-coumaryl)-glucopyranoside & Apigenin 7-*O*-(3"-*O*-*p*-coumaroyl)-glucopyranoside

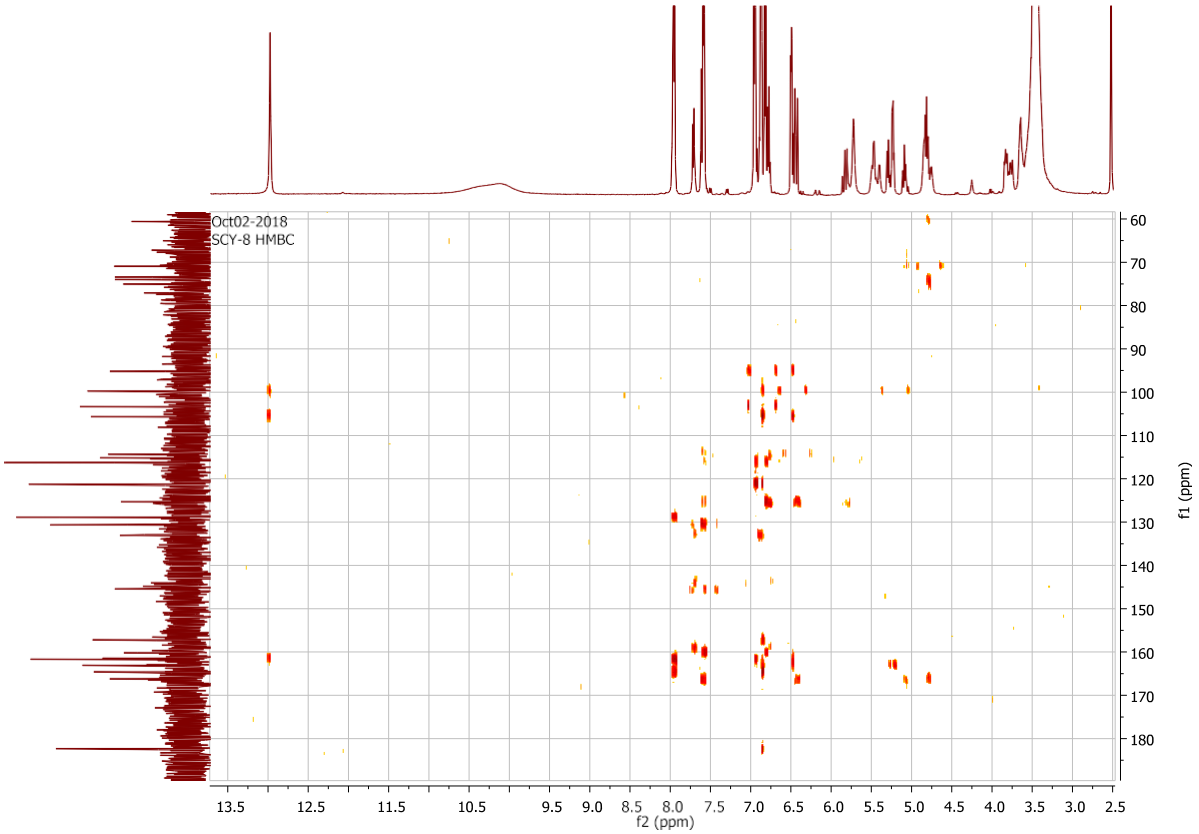


**Figure S56:** HMBC Spectrum of Compound **11 & 12** (Apigenin 7-*O*-(4"-*O*-*p*-coumaryl)-glucopyranoside & Apigenin 7-*O*-(3"-*O*-*p*-coumaroyl)-glucopyranoside)

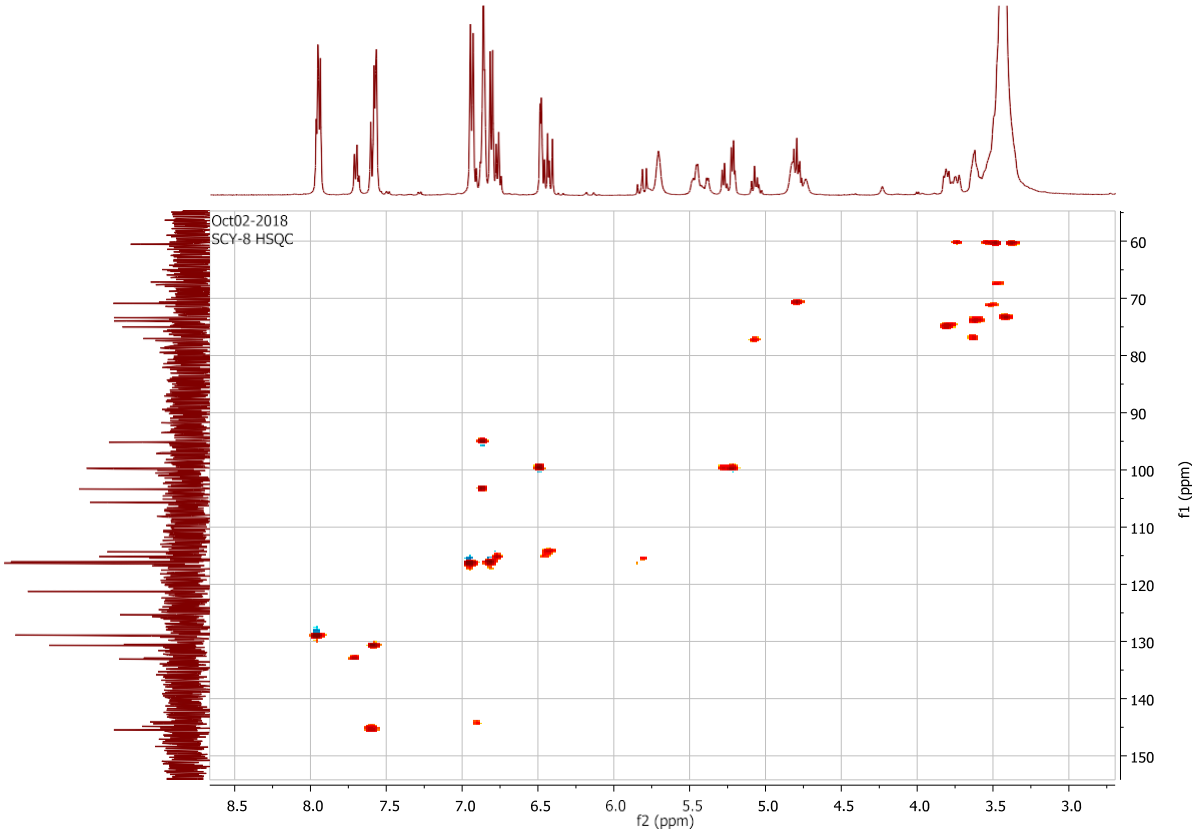


**Figure S57:** HSQC Spectrum of Compound **11 & 12** (Apigenin 7-*O*-(4"-*O*-*p*-coumaryl)-glucopyranoside & Apigenin 7-*O*-(3"-*O*-*p*-coumaroyl)-glucopyranoside)

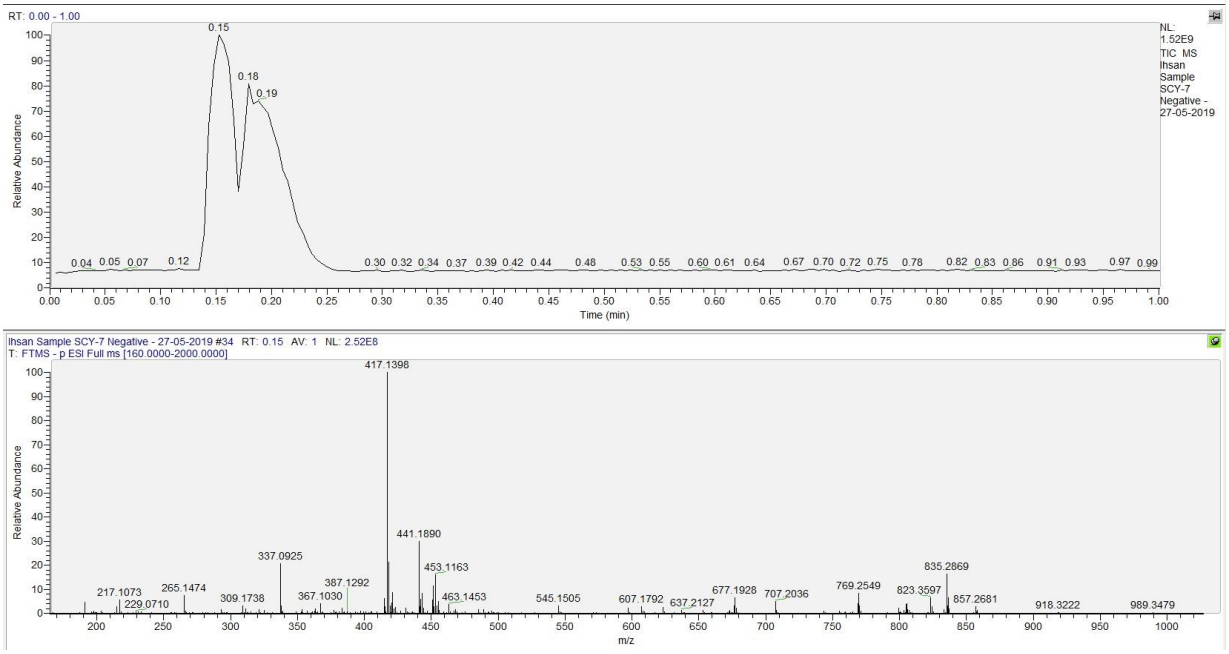


**Figure S58:** Negative- ion HRLCMS-MS Spectrum of Compound **13** (7-*O*-Acetyl-8-*epi*-loganic acid)

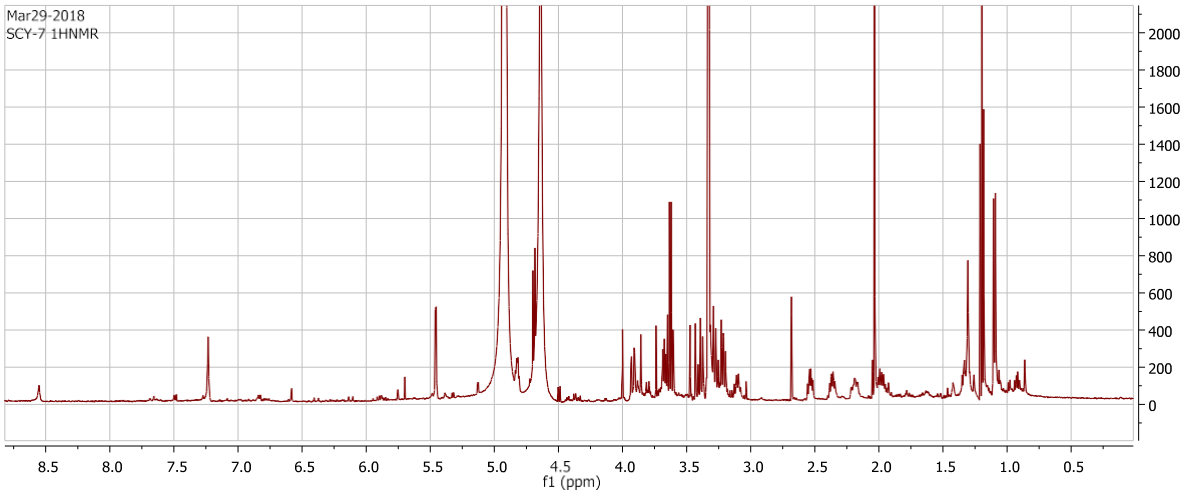


**Figure S59:** $^{1}$H-NMR (500 MHz, $CD_3OD$) Spectrum of Compound **13** (7-*O*-Acetyl-8-*epi*-loganic acid)

**Table 12:** The $^{1}H$ and $^{13}C$ NMR data of Compound **13** (7-*O*-Acetyl-8-*epi*-loganic acid) ($CD_3OD$; $\delta_H$ 500 MHz; $\delta_C$ 125 MHz)

| **C/H** | **DEPT** | **$\delta_C$** (ppm) | **$\delta_H$** (ppm), ***J*** (Hz) |
|---|---|---|---|
| 1 | CH | 94.1 | 5.44 d (4.3) |
| 3 | CH | 151.3 | 7.20 s |
| 4 | C | no | - |
| 5 | CH | 31.2 | 3.08 m |
| 6 | $CH_2$ | 37.4 | 2.17 m (β), 1.97 m (α) |
| 7 | CH | 81.7 | 4.80 m |
| 8 | CH | 41.2 | 2.34 m |
| 9 | CH | 41.5 | 2.52 ddd (4.3, 8.3, 12.5) |
| 10 | $CH_3$ | 12.8 | 1.08 d (7.4) |
| 11 | C | no | - |
| Glucose | | | |
| 1' | CH | 98.2 | 4.67 d (8.0) |
| 2' | CH | 73.4 | 3.20 dd (8.0, 9.0) |
| 3' | CH | 76.5 | 3.38 dd "t" (9.0) |
| 4' | CH | 70.2 | 3.26 dd "t" (9.0) |
| 5' | CH | 76.8 | 3.33 † |
| 6' | $CH_2$ | 61.1 | 3.90 dd (12.0, 1.9)<br>3.65 dd (12.0, 6.2) |
| $\underline{C}OCH_3$ | C | 171.8 | - |
| $CO\underline{C}H_3$ | $CH_3$ | 19.5 | 2.02 s |

†) *J* values could not be determined due to overlap.

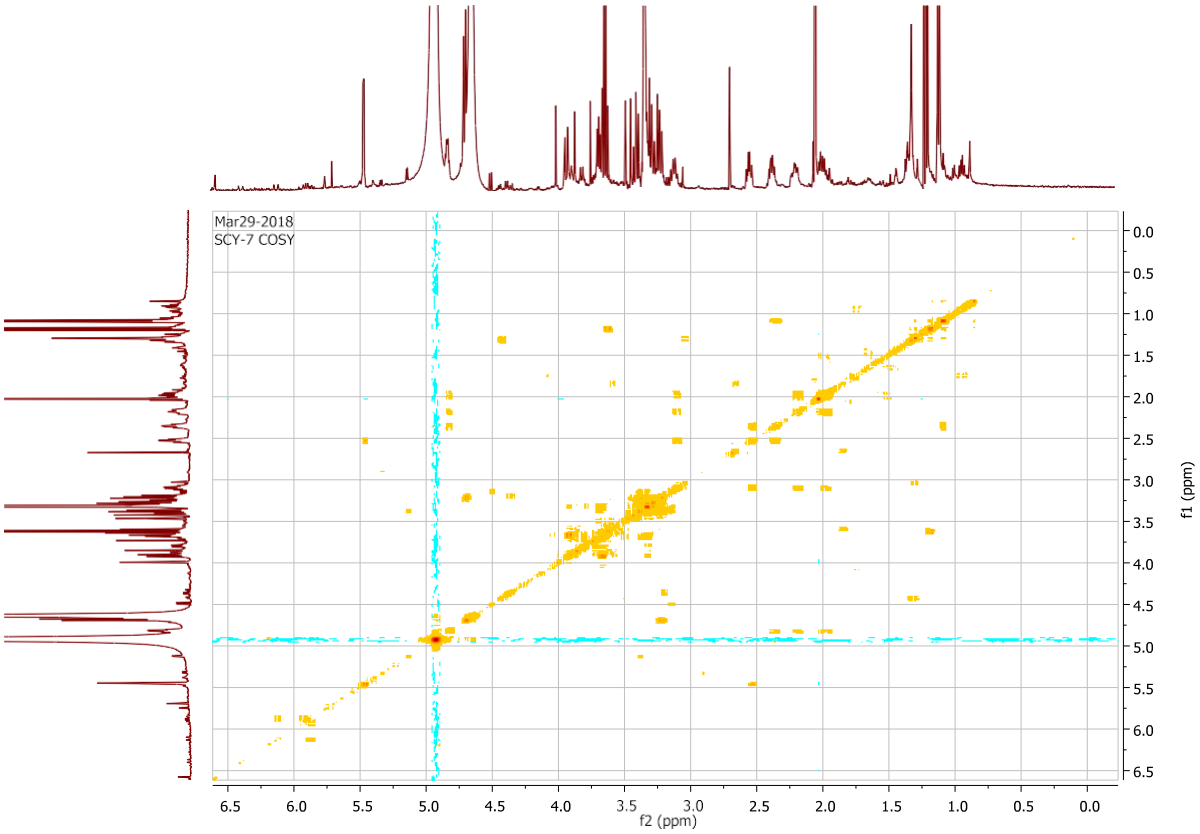


**Figure S60:** COSY Spectrum of Compound **13** (7-*O*-Acetyl-8-*epi*-loganic acid)