Supporting Information

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Phytochemical Investigation of Endemic Sideritis cypria Post

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



Figure S2: ¹H-NMR (500 MHz, CDCl₃) Spectrum of Compound 1&2 (Sidol & Isosidol)

C/H	DEPT	δ c (ppm)	б н (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	С	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	С	48.05	-
9	CH	44.63	2.37
10	С	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	С	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
<u>C</u> OCH ₃	С	171.82	-
$CO\underline{C}H_3$	CH_3	21.26	2.07 s

Table 1: The ¹H and ¹³C NMR data of Compound **1** (Sidol) (CDCl₃; δ_H 500 MHz; δ_C 125 MHz)

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

C/H	DEPT	$\delta_{\rm C}$ (ppm)	$\boldsymbol{\delta}_{\mathrm{H}}$ (ppm), \boldsymbol{J} (Hz)
1	CH_2	38.22	1.83†, 1.06†
2	CH_2	23.37	1.82†, 1.69†
3	СН	74.57	4.93 dd (11.8, 5.3)
4	С	38.51	-
5	СН	37.32	1.95 dd (11.6, 2.8)
6	CH_2	26.65	1.63†
7	СН	76.84	3.63†
8	С	53.20	-
9	CH	43.67	2.37
10	С	41.69	-
11	CH_2	18,49	1.49†
12	CH_2	24.89	1.50†, 1.70†
13	СН	45.01	2.31gs
14	CH_2	38.38	1.88, 1.37
15	СН	130.16	5.53 s
16	С	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
<u>C</u> OCH ₃	С	171.85	-
$CO\underline{C}H_3$	CH_3	21.26	2.07 s

Table 2: The ¹H and ¹³C NMR data of Compound **2** (Isosidol) (CDCl₃; δ_H 500 MHz; δ_C 125 MHz)

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



Figure S3: ¹³C-NMR (125 MHz, CDCl₃) 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: ¹H-NMR (500 MHz, CDCl₃) Spectrum of Compound 3&4 (Linearol & Isolinearol)

C/H	DEPT	δc (ppm)	$\boldsymbol{\delta}_{\mathrm{H}}$ (ppm), \boldsymbol{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	С	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	С	47.94	-
9	CH	50.21	1.46†
10	С	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	С	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
<u>C</u> OCH ₃	С	171.91	-
CO <u>C</u> H ₃	CH_3	21.20	2.09 s

Table 3: The ¹H and ¹³C NMR data of Compound **3** (Linearol) (CDCl₃; δ_H 500 MHz; δ_C 125 MHz)

 $^{\dagger})$ J values could not be determined due to overlap.

C/H	DEPT	$\delta_{\rm C}ppm$	$\delta_{\rm H}$ ppm, J (Hz)
1	CH ₂	38.14	1.85†, 0.98†
2	CH_2	26.71	1.70 - 1.60†
3	СН	72.18	3.52†
4	С	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	С	53.00	-
9	CH	43.83	1.33†
10	С	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	С	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
<u>C</u> OCH ₃	С	171.91	-
$CO\underline{C}H_3$	CH_3	21.20	2.09

Table 4: The ¹H and ¹³C NMR data of Compound 4 (Isolinearol) (CDCl₃; δ_H 500 MHz; δ_C 125 MHz)

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



Figure S11: ¹³C-NMR (125 MHz, CDCl₃) 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: ¹H-NMR (500 MHz, CD₃OD) Spectrum of Compound 5 (Verbascoside)

C/H	DEPT	δc (ppm)	δ _H (ppm), J (Hz)
Phenylethyl	С	131.5	_
alcohol 1	Ũ	10110	
2	CH	117.2	6.70 d (2.0)
3	С	146.7	-
4	С	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)
ß	СЦ	26.5	2.70 ddd 'dt'' (7.0, 8.3)
p Glucose 1'		104.3	2.79 ddd dd $(7.0, 8.3)$
2'		76.1	4.50 d (0.0)
2 3'	СН	70.1 81 7	3.80 dd"+" (0.0)
3 1'	СН	70.5	4.92 dd''t'' (9.0)
+ 5'		74.6	4.92 uu t (9.0)
5		74.0 62.4	2.62+ 2.52+
U Dhomnooo 1"	CH_2	02.4	5.02[, 5.32]
	СП	105.1	3.19 u (1.7)
2	СЦ	72.2	3.52 dd (1.7, 3.2)
3 4''		71.9	3.36 dd (3.2, 9.0)
4 5"		73.7	5.29 dd t (9.0)
J 6''	СП	10.4	1.00 4 (6.2
U Coffeie acid 1'''	$C\Pi_3$	10.4	1.09 d (0.2
		127.7	-
2	Сн	115.5	7.05 ŭ (2.0)
3 4'''	C	146.9	-
4	CU	149.9	-
5	CH	110.0	6.78 d (8.2)
0	CH	123.2	6.95 dd (8.2 / 2.0)
α	CH	114.8	6.2/d(16.0)
β'	СН	148.1	7.58 d (16.0)
C=O	С	168.3	-

Table 5: The ¹H and ¹³C NMR data of Compound 5 (Verbascoside) (CD₃OD; δ_H 500 MHz; δ_C 125 MHz)

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



Figure S20: COSY Spectrum of Compound 5 (Verbascoside)



Figure S21: ¹H-NMR (500 MHz, CD₃OD) Spectrum of Compound 6 (Lavandulifolioside)

<u>C/H</u>	DEPT	ð _C (ppm)	δH (ppm), J (Hz)
Phenylethyl	С	131.5	-
	CU	1165	7.05.1(2.0)
2	СН	116.5	7.05 d (2.0)
3	C	146.1	-
4	С	144.7	-
5	CH	117.1	6.77 d (8.0)
6	СН	121.3	6.95 dd (8.0 / 2.0)
α	CH_2	72.3	4.04 ddd "dt" (7.0, 8.3) 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""	С	127.6	-
2""	CH	114.7	7.05 d (2.0)
3""	С	146.8	-
4""	С	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	С	168.3	-

Table 6: The ¹H and ¹³C NMR data of Compound 6 (Lavandulifolioside) (CD₃OD; δ_H 500 MHz; δ_C 125 MHz)

 \dagger) J values could not be determined due to overlap.



Figure S22: ¹³C-NMR (125 MHz, CD₃OD) 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: ¹H-NMR (500 MHz, CD₃OD) Spectrum of Compound 7 (Leonoside A)

С/Н	DEPT	δ _C (nnm)	$\delta_{\rm H}$ (npm) I (Hz)
Phenylethyl alcohol			on (ppm), 9 (112)
1	С	131.4	-
2	CH	116.3	7.19 d (2.0)
3	С	146.0	-
4	С	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) 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""	С	127.6	-
2""	CH	111.7	6.72 d (2.0)
3""	С	149.3	-
4''''	С	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	С	168.3	-
OCH ₃	CH_3	56.4	3.88 s

Table 7: The 1H and ^{13}C NMR data of Compound 7 (Leonoside A) (CD₃OD; δ_H 500 MHz; δ_C 125 MHz)



Figure S30: ¹³C-NMR (125 MHz, CD₃OD) 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: ¹H-NMR (500 MHz, CD₃OD) Spectrum of Compound 8 (Leucoseptoside A)

C/H	DEPT	δ _C (ppm)	δH (ppm), J (Hz)
Fenylethyl alcohol 1	С	131.4	-
2	CH	117.1	6.73 d (1.8)
3	С	146.0	-
4	С	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) 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"	С	127.6	-
2'''	CH	111.7	7.20 d (1.8)
3'''	С	149.3	-
4'''	С	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	С	168.3	-
OMe	CH_3	56.4	3.89 s

Table 8: The ¹H and ¹³C NMR data of Compound 8 (Leucoseptoside A) (CD₃OD; δ_H 500 MHz; δ_C 125 MHz)



Figure S35: ¹³C-NMR (125 MHz, CD₃OD) 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: ¹H-NMR (500 MHz, DMSO-d₆) Spectrum of Compound **9** (Apigenin 7-*O*-glucopyranoside)

C/H	DEPT	δc (ppm)	δ н (ppm), J (Hz)
Apigenin 2	С	164.7	-
3	СН	103.6	6.87 s
4	С	182.5	-
5	С	161.8	-
6	CH	99.9	6.45 d (1.8)
7	С	163.4	-
8	CH	95.3	6.84 d (1.8)
9	С	157.4	-
10	С	105.8	-
1'	С	121.5	-
2'	CH	129.1	7.96 d (8.9)
3'	СН	116.5	6.95 d (8.9)
4′	С	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)

Table 9: The ¹H and ¹³C NMR data of Compound **9** (Apigenin 7-*O*-glucopyranoside) (DMSO-d₆; δ_H 500 MHz; δ_C 125 MHz)



Figure S40: ¹³C-NMR (A) + DEPT-135 (B) (125 MHz, DMSO-d₆) 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 \rightarrow 2)-glucopyranoside])



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



Figure S46: ¹H-NMR (500 MHz, DMSO-d₆) Spectrum of Compound **10** (Isoscutellarein-7-O-[6'''-O-acetyl-allopyranosyl-(1 \rightarrow 2)-glucopyranoside])

C/H	DEPT	δ c (ppm)	б н (ppm), J (Hz)
Isoscutellarein 2	С	164.5	-
3	CH	99.8	6.84 s
4	С	182.7	-
5	С	152.0	-
6	CH	103.1	6.70 s
7	С	151.0	-
8	С	128.0	-
9	С	144.0	-
10	С	100.0	-
1'	С	121.6	-
2'	CH	129.1	7.99 d (8.8)
3'	CH	116.5	6.96 d (8.8)
4′	С	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 †
<u><i>C</i></u> OCH ₃	С	171.8	-
CO <u>C</u> H ₃	CH_3	21.1	1.87 s

Table 9: The ¹H and ¹³C NMR data of Compound **10** (Isoscutellarein-7-O-[6'''-O-acetyl-allopyranosyl-
(1 \rightarrow 2)-glucopyranoside]) (DMSO-d₆; δ_H 500 MHz; δ_C 125 MHz)



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



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



Figure S49: HSQC Spectrum of Compound 10 (Isoscutellarein-7-O-[6'''-O-acetyl-allopyranosyl-(1 \rightarrow 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*-coumaryl)-glucopyranoside)



Figure S52: ¹H-NMR (500 MHz, DMSO-d₆) Spectrum of Compound **11 & 12** (Apigenin 7-*O*-(4"-*O*-*p*-coumaryl)- glucopyranoside & Apigenin 7-*O*-(3"-*O*-*p*-coumaroyl)glucopyranoside)

		11		12		
C/H	DEPT	δc (ppm)	δ н (ppm), J (Hz)	δc (ppm)	δ н (ppm), J (Hz)	
Apigenin 2	С	164.7	-			
3	CH	103.6	6.86 s			
4	С	182.5	-			
5	С	161.8	-			
6	CH	99.8	6.48 d (1.8)			
7	С	163.4	-			
8	CH	95.4	6.86 d (1.8)			
9	С	157.4	-			
10	С	105.8	-			
1'	С	121.5	-			
2'	CH	129.1	7.95 d (8.5)			
3'	CH	116.5	6.94 d (8.5)			
4'	С	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†	
<i>p</i> - coumaryl 1'''	С	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'''	С	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	С	166.4	-	166.7	-	

Table 10: The ¹H and ¹³C NMR data of Compound **11&12** (Apigenin 7-O-(4"-O-p-coumaryl)-glucopyranoside & Apigenin 7-O-(3"-O-p-coumaroyl)-glucopyranoside) (DMSO-d₆; δ_{H} 500 MHz; δ_{C} 125 MHz)



Figure S53: ¹³C-NMR (125 MHz, DMSO-d₆) Spectrum of Compound **11 & 12** (Apigenin 7- *O*-(4"-*O*-*p*-coumaryl)- glucopyranoside & Apigenin 7-*O*-(3"-*O*-*p*-coumaryl)- 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: ¹H-NMR (500 MHz, CD₃OD) Spectrum of Compound **13** (7-*O*-Acetyl-8-*epi*-loganic acid)

C/H	DEPT	$\delta_{\rm C}$ (ppm)	δ_{H} (ppm), \boldsymbol{J} (Hz)
1	СН	94.1	5.44 d (4.3)
3	CH	151.3	7.20 s
4	С	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	СН	41.5	2.52 ddd (4.3, 8.3, 12.5)
10	CH_3	12.8	1.08 d (7.4)
11	С	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) 3.65 dd (12.0, 6.2)
<u>C</u> OCH ₃	С	171.8	-
CO <u>C</u> H ₃	CH_3	19.5	2.02 s

Table 12: The ¹H and ¹³C NMR data of Compound **13** (7-O-Acetyl-8-epi-loganic acid) (CD₃OD; δ_H 500 MHz; δ_C 125 MHz)

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



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