

## Supporting Information

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### Rapid Profiling and Identification of Triterpene Saponins in Three Different *Cephalaria* Species by UPLC-ESI-MS/MS

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Contents	Page
S 1: Validation Results of LC-MS/MS Measurements.	8
S 2: Identification of saponins by UPLC-ESI-MS/MS.	9
S 3: Chromatograms of Decaisoside D compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	11
S 4: Chromatograms of Scoposide C compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	11
S 5: Chromatograms of Gazipashoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	12
S 6: Chromatograms of Aristatoside C compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	12
S 7: Chromatograms of Aristatoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	13

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<b>S 8:</b> Chromatograms of Aristatoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	13
<b>S 9:</b> Chromatograms of $\alpha$ -Hederin compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	14
<b>S 10:</b> Chromatograms of Elmalienoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	14
<b>S 11:</b> Chromatograms of Sapindoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	15
<b>S 12:</b> Chromatograms of 3-O- $\alpha$ -L-rhamnopyranosyl-(1→2)- $\alpha$ -L-arabinopyranosyl hederagenin 28-O- $\beta$ -D-glucopyranosyl ester compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	15
<b>S 13:</b> Chromatograms of Macranthoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	16
<b>S 14:</b> Chromatograms of 3-O- $\beta$ -D-glucopyranosyl-(1→3)- $\alpha$ -L-rhamnopyranosyl-(1→2)- $\alpha$ -L-arabinopyranosyl hederagenin 28-O- $\beta$ -D- glucopyranosyl ester compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	16
<b>S 15:</b> Chromatograms of Elmalienoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	17
<b>S 16:</b> Chromatograms of Dipsacoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	17
<b>S 17:</b> Chromatograms of Macranthoidin A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	18
<b>S 18:</b> Chromatograms of Elmalienoside C compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	18
<b>S 19:</b> Chromatograms of Sapindoside C compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	19
<b>S 20:</b> Chromatograms of $\beta$ -Sitosterol-Glucoside compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	19
<b>S 21:</b> Chromatograms of Scoposide D compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	20
<b>S 22:</b> Chromatograms of Scoposide E compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	20
<b>S 23:</b> Chromatograms of Scoposide G compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	21

<b>S 24:</b> Chromatograms of Davisianoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	21
<b>S 25:</b> Chromatograms of Scoposide A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	22
<b>S 26:</b> Chromatograms of Lycicoside II compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	22
<b>S 27:</b> Chromatograms of Scoposide F compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	23
<b>S 28:</b> Chromatograms of Gazipashoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	23
<b>S 29:</b> Chromatograms of Scoposide B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	24
<b>S 30:</b> Chromatograms of Decaisoside E compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. hirsuta</i> .	24
<b>S 31:</b> Chromatograms of Macranthoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. elazigenis</i> var. <i>elazigenis</i> .	25
<b>S 32:</b> Chromatograms of $\beta$ -Sitosterol-Glucoside compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. elazigenis</i> var. <i>elazigenis</i> .	25
<b>S 33:</b> Chromatograms of Scoposide A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. elazigenis</i> var. <i>elazigenis</i> .	26
<b>S 34:</b> Chromatograms of Scoposide F compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. elazigenis</i> var. <i>elazigenis</i> .	26
<b>S 35 :</b> Chromatograms of Decaisoside D compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	27
<b>S 36:</b> Chromatograms of $\alpha$ -Hederin compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	27
<b>S 37:</b> Chromatograms of Elmalienoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	28
<b>S 38:</b> Chromatograms of Sapindoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	28
<b>S 39:</b> Chromatograms of 3-O- $\alpha$ -L-rhamnopyranosyl-(1→2)- $\alpha$ -L-arabinopyranosyl hederagenin 28-O- $\beta$ -D-glucopyranosyl ester compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	29
<b>S 40:</b> Chromatograms of Macranthoside compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	29

<b>S 41:</b> Chromatograms of 3-O- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3)- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -L-arabinopyranosyl hederagenin 28-O- $\beta$ -D- glucopyranosyl ester compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	30
<b>S 42:</b> Chromatograms of Elmalienoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	30
<b>S 43:</b> Chromatograms of Dipsacoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	31
<b>S 44</b> Chromatograms of Macranthoidin A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution <i>C. procera</i> .	31
<b>S 45</b> Chromatograms of Elmalienoside C compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	32
<b>S 46:</b> Chromatograms of Sapindoside C compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	32
<b>S 47:</b> Chromatograms of $\beta$ -Sitosterol-Glucoside compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	33
<b>S 48:</b> Chromatograms of Macranthoidin B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	33
<b>S 49:</b> Chromatograms of Scoposide D compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	34
<b>S 50:</b> Chromatograms of Scoposide G compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	34
<b>S 51:</b> Chromatograms of Scoposide A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	35
<b>S 52:</b> Chromatograms of Lycicoside II compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	35
<b>S 53:</b> Chromatograms of Scoposide F compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	36
<b>S 54:</b> Chromatograms of Gazipashoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	36
<b>S 55:</b> Chromatograms of Scoposide B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	37
<b>S 56:</b> Chromatograms of Decaisoside E compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in <i>C. procera</i> .	37
<b>S 57:</b> Chromatograms of Davisianoside A compound obtained by UPLC–ESI-MS-MS	

in the positive ion mode for standard solution (0.100 mg/L).	38
<b>S 58:</b> Chromatograms of Aytachoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	38
<b>S 59:</b> Chromatograms of Anemoclemoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	38
<b>S 60:</b> Chromatograms of Akebia Saponin D compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	39
<b>S 61:</b> Chromatograms of Gazipashoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	39
<b>S 62:</b> Chromatograms of Aristatoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	39
<b>S 63:</b> Chromatograms of Cilicicoside I compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	40
<b>S 64:</b> Chromatograms of Macranthoidin B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	40
<b>S 65:</b> Chromatograms of Aristatoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	40
<b>S 66:</b> Chromatograms of Decaisoside E compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	41
<b>S 67:</b> Chromatograms of Macranthoidin A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	41
<b>S 68:</b> Chromatograms of Elmalienoside C compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	41
<b>S 69:</b> Chromatograms of Elmalienoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	42
<b>S 70:</b> Chromatograms of Balansoid D compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	42
<b>S 71:</b> Chromatograms of Dipsacoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	42
<b>S 72:</b> Chromatograms of Elmalienoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	43
<b>S 73:</b> Chromatograms of Balansoid B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	43
<b>S 74:</b> Chromatograms of Gazipashoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	43
<b>S 75:</b> Chromatograms of Scoposide C compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	44

<b>S 76:</b> Chromatograms of Balansoid C compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution(0.100 mg/L).	44
<b>S 77:</b> Chromatograms of - 3-O-β-D-glucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl hederagenin 28-O-β-D- glucopyranosyl ester compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	44
<b>S 78:</b> Chromatograms of Scoposide B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	45
<b>S 79:</b> Chromatograms of Decaisoside D compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	45
<b>S 80:</b> Chromatograms of 3-O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl hederagenin 28-O-β-D-glucopyranosyl ester compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	45
<b>S 81:</b> Chromatograms of Aristatoside C compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	46
<b>S 82:</b> Chromatograms of Scoposide F compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	46
<b>S 83:</b> Chromatograms of Sapindoside C compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	46
<b>S 84:</b> Chromatograms of Scoposide G compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	47
<b>S 85:</b> Chromatograms of Scoposide A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	47
<b>S 86:</b> Chromatograms of α-Hederin compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	47
<b>S 87:</b> Chromatograms of Scoposide D compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	48
<b>S 88:</b> Chromatograms of Isacoside compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	48
<b>S 89:</b> Chromatograms of Sapindoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	48
<b>S 90:</b> Chromatograms of Lycicoside II compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	49
<b>S 91:</b> Chromatograms of Macranthoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	49
<b>S 92:</b> Chromatograms of Davisianoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	49
<b>S 93:</b> Chromatograms of Balansoid A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	50

<b>S 94:</b> Chromatograms of Hederagenin compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	50
<b>S 95:</b> Chromatograms of Scoposide E compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	50
<b>S 96:</b> Chromatograms of $\beta$ -Sitosterol glucoside compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).	51

## S 1. Validation Results of LC-MS/MS Measurements

No	Compounds	Purity of Reference Compounds(%)	Linear regression equation	Correlation coefficients	LOD (µg/kg)	LOQ (µg/kg)	RSD (%)	Mean Recovery (%)
1	Davisianoside A	97.5	$y = 28284x - 124.09$	0.9997	3.47	11.56	7.8	94.2
2	Aytachoside A	95.9	$y = 51167x + 931.4$	0.9995	0.04	0.14	4.5	95.8
3	Anemocleumoside A	99.2	$y = 32238x - 239.51$	0.9997	1.96	6.52	2.6	94.1
4	Akebia Saponin D	99.7	$y = 353893x + 4581.7$	0.9995	0.17	0.57	6.8	96.4
5	Gazipashoside B	100.0	$y = 20045x + 82.039$	0.9999	0.05	0.16	6.3	91.2
6	Aristatoside B	99.2	$y = 25037x - 202.75$	0.9989	0.16	0.54	6.2	94.6
7	Cilicicoside I	99.7	$y = 18845x - 93.366$	0.9995	0.32	1.07	1.5	100.2
8	Macranthoidin B	96.7	$y = 8891.6x + 89$	0.9998	0.05	0.16	3.8	94.6
9	Aristatoside A	98.8	$y = 26522x - 71.643$	0.9991	0.77	2.57	8.5	99.1
10	Decaisoside E	99.8	$y = 182132x - 174$	0.9999	0.02	0.06	2.9	92.1
11	Macranthoidin A	99.8	$y = 151828x - 963.37$	0.9994	0.51	1.71	7.1	95.7
12	Elmalienoside C	100.0	$y = 47906x + 307.24$	0.9998	0.41	1.35	2.4	94.8
13	Elmalienoside A	99.6	$y = 179516x + 773.8$	0.9999	0.06	0.21	3.9	96.8
14	Balansoid D	97.5	$y = 144694x + 186.52$	0.9997	0.08	0.28	4.4	96.1
15	Dipsacoside B	99.2	$y = 105452x - 589.63$	0.9996	0.31	1.02	7.7	101.9
16	Elmalienoside B	100.0	$y = 21637x - 140.58$	0.9998	1.94	6.47	8.7	105.9
17	Balansoid B	99.9	$y = 120421x + 368.67$	0.9999	0.23	0.75	8.9	92.6
18	Gazipashoside A	99.9	$y = 142368x - 1421.6$	0.9997	1.08	3.60	5.8	91.3
19	Scoposide C	99.6	$y = 10400x + 43.638$	0.9999	0.30	1.00	8.9	90.8
20	Balansoid C	98.5	$y = 45076x - 0.6019$	0.9999	0.04	0.15	8.2	91.1
21	Comp1*	100.0	$y = 125553x - 678.94$	0.9995	1.90	6.33	4.0	97.8
22	Scoposide B	99.9	$y = 69463x - 409.19$	0.9987	0.61	2.04	7.2	95.2
23	Decaisoside D	99.0	$y = 50598x - 259.08$	0.9996	5.56	18.55	8.0	96.2
24	Comp2*	99.7	$y = 124869x - 130.93$	0.9997	1.86	6.20	1.2	95.2
25	Aristatoside C	93.7	$y = 7474.1x - 26.409$	0.9996	6.16	20.53	6.0	92.1
26	Scoposide F	99.7	$y = 70425x + 410.37$	0.9998	0.87	2.91	5.1	93.0
27	Sapindoside C	99.8	$y = 14230x + 19.968$	0.9999	3.19	10.64	5.2	98.9
28	Scoposide G	99.6	$y = 6524.1x - 8.9959$	0.9999	0.37	1.22	4.5	97.1
29	Scoposide A	99.8	$y = 4902.3x - 0.7102$	0.9999	0.30	1.00	4.7	91.3
30	$\alpha$ -Hederin	100.0	$y = 25324x - 85.064$	0.9998	2.59	8.62	7.0	94.6
31	Scoposide D	92.1	$y = 102197x + 624.96$	0.9974	0.10	0.35	7.1	98.8
32	Isacoside	96.5	$y = 17258x + 149.08$	0.9993	4.53	15.10	2.4	91.3
33	Sapindoside B	100.0	$y = 8193.6x - 16.119$	0.9998	1.05	3.48	3.4	98.7
34	Lycicoside II	98.7	$y = 100698x - 70.859$	0.9998	0.52	1.75	4.0	100.5
35	Macranthoside A	98.6	$y = 35428x - 4.7529$	0.9999	0.72	2.39	4.5	100.9
36	Davisianoside B	97.6	$y = 3496.6x + 7.6733$	0.9998	2.88	9.59	6.2	92.5
37	Balansoid A	99.3	$y = 18248x - 48.888$	0.9999	1.82	6.08	8.4	90.0
38	Hederagenin	96.6	$y = 4035.8x - 9.3593$	0.9998	0.29	0.96	4.9	92.6
39	Scoposide E	99.4	$y = 854.66x - 6.1706$	0.9997	1.10	3.66	2.4	98.8



40  $\beta$ -Sitosterol glucoside 99.0  $y = 123352x - 186.79$  0.9999 0.09 0.28 4.2 97.9

Comp1\* : 3-O- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3)- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -L-arabinopyranosyl hederagenin 28-O- $\beta$ -D- glucopyranosyl ester

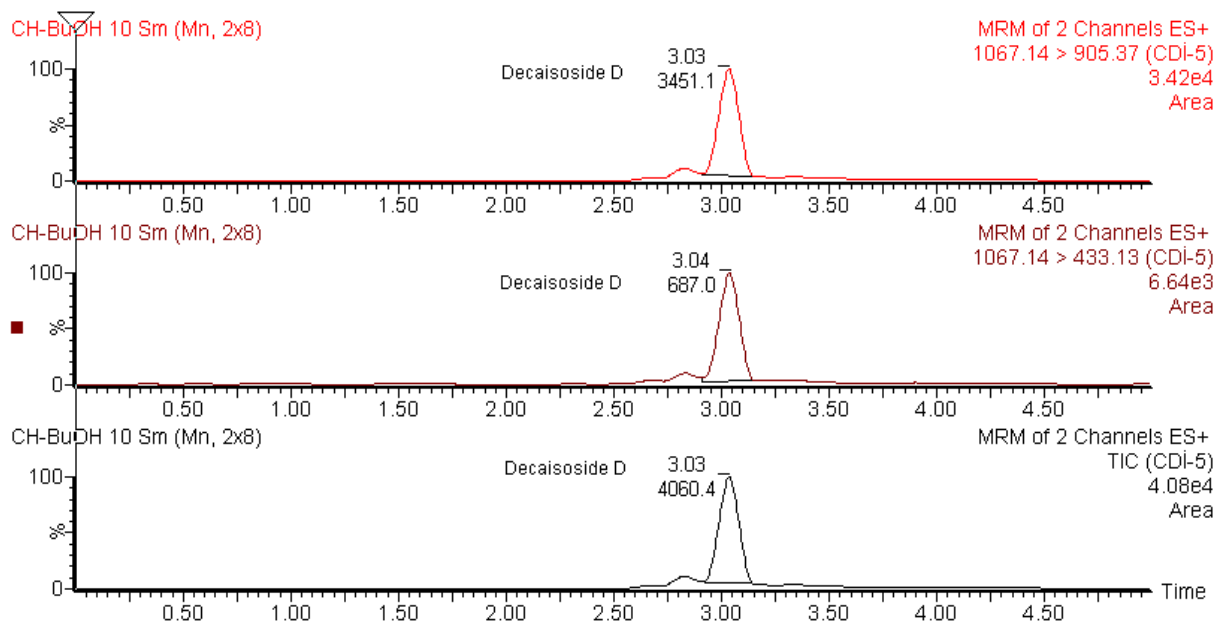
Comp2\* : 3-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -L-arabinopyranosyl hederagenin 28-O- $\beta$ -D-glucopyranosyl ester

## S 2. Identification of saponins by UPLC-ESI-MS/MS.

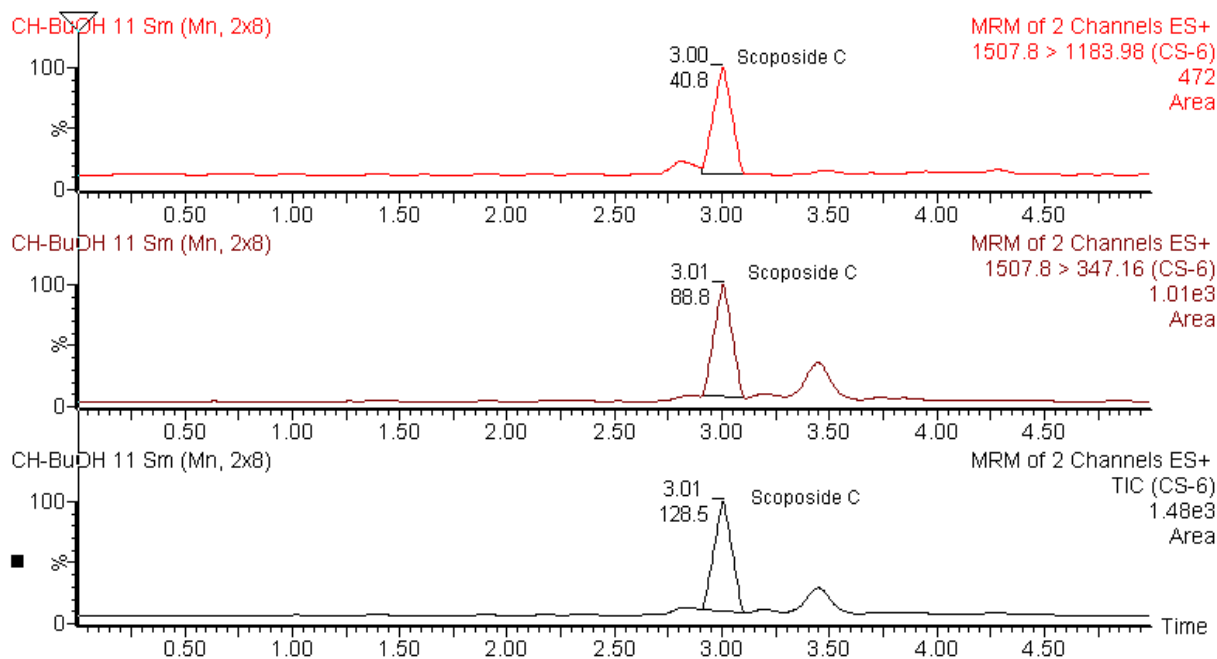
Peak No	Compounds and Related References	RT (min)	Molecular Formula	Observed Precursor Ions (m/z)	Calculated Ions (m/z)	Observed Transition Ions (m/z)	Cone Energy (V)	Collision Energy (V)
1	Davisianoside A [19]	1.89	$C_{65}H_{106}O_{31}Na_2$	1406.0	1428.6508	347.12	100	80
						1081.5	100	70
2	Aytachoside A [20]	2.05	$C_{59}H_{96}O_{26}Na$	1243.61	1243.6082	477.15	100	80
						1081.44	100	65
3	Anemocleboside A [25]	2.7	$C_{35}H_{56}O_8$	627.16	604.3975	537.3	65	40
						583.43	65	40
4	Akebia saponin D [26]	2.76	$C_{47}H_{76}O_{18}$	951.25	929.10	347.16	100	60
						627.48	100	55
5	Gazipashoside B [23]	2.82	$C_{64}H_{103}O_{31}$	1391.96	1367.6483	1067.81	120	75
						346.96	120	80
6	Aristatoside B [22]	2.82	$C_{70}H_{114}O_{35}Na$	1537.70	1537.7033	347.16	100	85
						1213.49	100	70
7	Cilicicoside I [18]	2.83	$C_{71}H_{117}O_{36}Na$	1568.0	1568.20	347.16	100	80
						1244.26	100	70
8	Macranthoidin B [27]	2.84	$C_{65}H_{106}O_{32}$	1421.14	1399.5179	1097.55	120	70
						493.10	120	75
9	Aristatoside A [22]	2.84	$C_{71}H_{116}O_{36}Na$	1567.7	1567.7139	347.19	100	90
						639.13	100	90
10	Decaisoside E [28]	2.87	$C_{58}H_{94}O_{26}Na$	1229.87	1229.5931	432.99	100	75
						346.92	100	75
11	Macranthoidin A [29]	2.88	$C_{59}H_{96}O_{27}Na$	1259.60	1259.6031	935.40	120	70
						347.06	120	70
12	Elmalienoside C [4]	2.89	$C_{58}H_{94}O_{26}Na$	1230.50	1229.5926	905.87	130	70
						347.39	130	80
13	Elmalienoside A [4]	2.91	$C_{59}H_{96}O_{27}Na$	1259.60	1259.6031	935.39	160	70
						346.91	160	75
14	Balansoid D [30]	2.91	$C_{64}H_{104}O_{30}Na$	1375.60	1375.6505	347.21	130	75
						1051.48	130	70
15	Dipsacoside B [31]	2.92	$C_{53}H_{86}O_{22}Na$	1097.55	1097.5503	773.08	120	65
						346.94	120	65
16	Elmalienoside B [4]	2.92	$C_{53}H_{86}O_{22}Na$	1098.56	1097.55	774.15	60	60
						347.84	60	72
17	Balansoid B [30]	2.93	$C_{64}H_{104}O_{30}Na$	1375.60	1375.6505	347.10	130	80
						1051.4	130	70
18	Gazipashoside A [23]	3.00	$C_{64}H_{103}O_{30}$	1375.46	1351.654	347.19	130	75
						1051.55	130	60
19	Scoposide C [5]	3.01	$C_{69}H_{112}O_{34}Na$	1507.80	1507.6933	347.16	130	80
						1183.98	130	70
20	Balansoid C	3.03	$C_{58}H_{94}O_{25}Na$	1213.60	1213.5976	447.19	130	73

	[30]					1051.19	130	70
21	Comp 1*	3.03	C <sub>53</sub> H <sub>86</sub> O <sub>22</sub> Na	1097.55	1097.5503	935.39	100	60
	[32]					330.96	100	70
22	Scoposide B	3.04	C <sub>64</sub> H <sub>104</sub> O <sub>30</sub> Na	1375.66	1375.6505	1051.37	100	70
	[5]					347.03	100	80
23	Decaisoside D	3.05	C <sub>52</sub> H <sub>84</sub> O <sub>21</sub>	1067.14	1045.2367	433.13	130	65
	[28]					905.37	130	55
24	Comp 2*	3.07	C <sub>47</sub> H <sub>76</sub> O <sub>17</sub> Na	935.49	935.4975	773.48	110	55
	[33]					184.97	110	60
25	Aristatoside C	3.07	C <sub>57</sub> H <sub>92</sub> O <sub>25</sub> Na	1200.09	1199.582	595.15	120	70
	[22]					1156.12	120	60
26	Scoposide F	3.09	C <sub>58</sub> H <sub>93</sub> O <sub>25</sub>	1213.50	1189.6011	889.30	100	60
	[24]					346.97	100	75
27	Sapindoside C	3.10	C <sub>52</sub> H <sub>84</sub> O <sub>21</sub> Na	1068.40	1045.2367	1024.26	150	60
	[34]					595.66	150	60
28	Scoposide G	3.15	C <sub>58</sub> H <sub>94</sub> O <sub>25</sub> Na	1213.59	1213.5976	1051.19	100	60
	[24]					346.88	100	75
29	Scoposide A	3.17	C <sub>53</sub> H <sub>101</sub> O <sub>20</sub> Na	1082.50	1057.6892	757.59	120	60
	[5]					347.51	120	65
30	$\alpha$ -Hederin	3.2	C <sub>41</sub> H <sub>66</sub> O <sub>12</sub> Na	773.44	773.444	729.04	100	45
	[35]					583.46	100	50
31	Scoposide D	3.22	C <sub>52</sub> H <sub>84</sub> O <sub>20</sub> Na	1051.54	1051.5448	889.40	120	55
	[5]					845.47	120	55
32	Isacoside	3.22	C <sub>64</sub> H <sub>104</sub> O <sub>30</sub> Na	1375.6	1375.6505	625.14	100	90
	[21]					771.40	100	85
33	Sapindoside B	3.24	C <sub>46</sub> H <sub>74</sub> O <sub>16</sub> Na	905.48	905.4869	861.25	110	55
	[36]					583.34	110	55
34	Lycicoside II	3.24	C <sub>52</sub> H <sub>83</sub> O <sub>20</sub> Na	1051.70	1027.5483	889.29	120	55
	[18]					301.07	120	65
35	Macranthoside A	3.26	C <sub>47</sub> H <sub>76</sub> O <sub>17</sub> Na	935.50	935.4975	462.93	150	60
	[37]					330.95	150	60
36	Davisianoside B	3.26	C <sub>53</sub> H <sub>86</sub> O <sub>21</sub> Na	1082.61	1081.5554	609.34	100	65
	[19]					477.35	100	65
37	Balansoid A	3.27	C <sub>52</sub> H <sub>84</sub> O <sub>20</sub> Na	1051.80	1051.5448	447.12	120	60
	[30]					579.12	120	60
38	Hederagenin	3.36	C <sub>30</sub> H <sub>48</sub> O <sub>4</sub>	495.30	472.6997	451.40	70	24
	[32]					-	-	-
39	Scoposide E	3.43	C <sub>46</sub> H <sub>73</sub> O <sub>15</sub>	890.47	865.4949	845.87	100	50
	[5]					-	-	-
40	$\beta$ -Sitosterol glucoside [38]	3.96	C <sub>35</sub> H <sub>60</sub> O <sub>6</sub>	1175.78*	576.85	599.03	100	50
						202.92	100	60

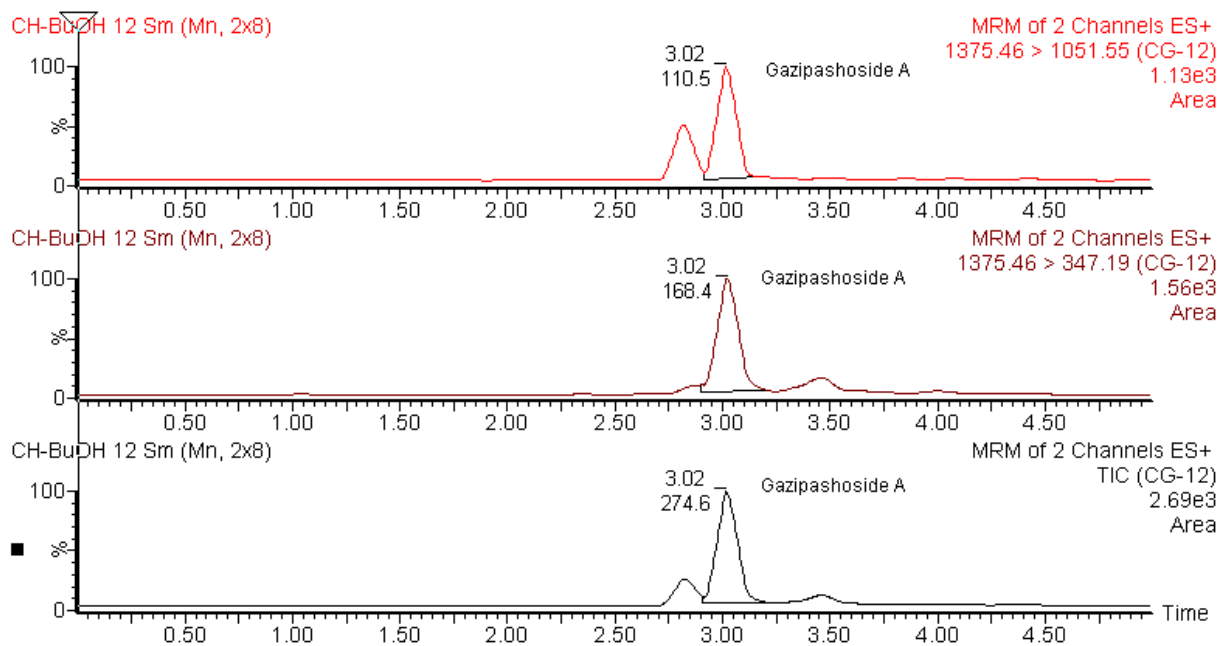
\*Dimeric molecular weight



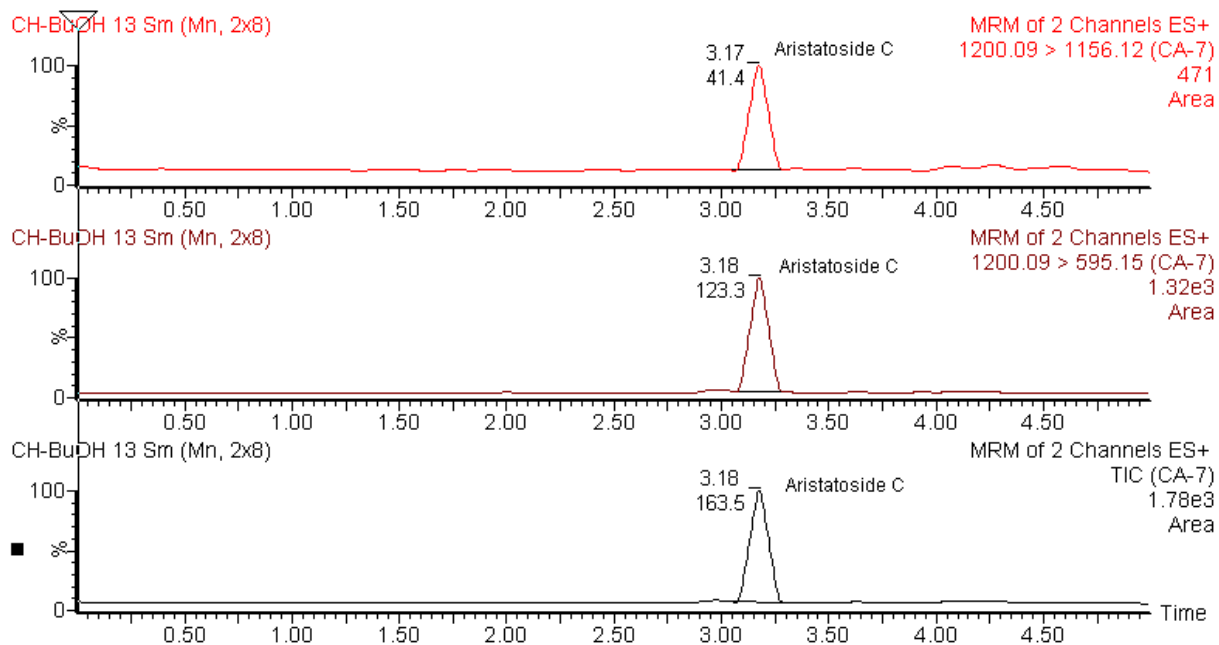
**S 3.** Chromatograms of Decaisoside D ( $m/z$ : 1067.14  $\rightarrow$  905.37, 1067.14  $\rightarrow$  433.13 and TIC), compound obtained by UPLC–ESI–MS–MS in the positive ion mode for crude extract solution in *C. hirsuta*.



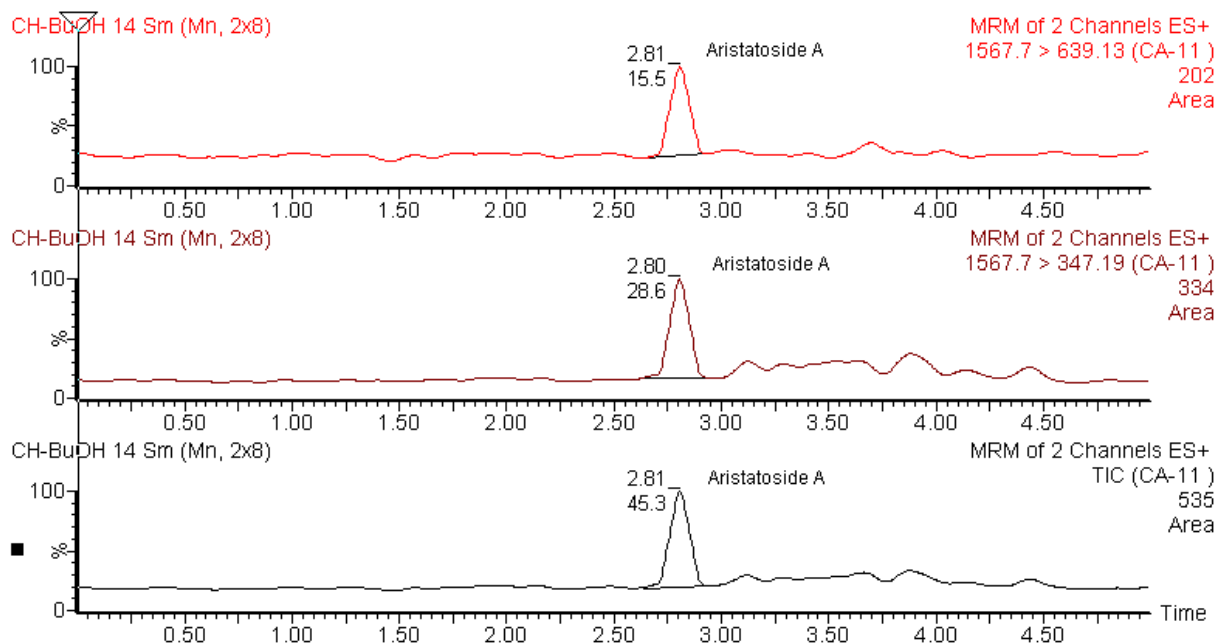
**S 4.** Chromatograms of Scoposide C ( $m/z$ : 1507.80  $\rightarrow$  11833.98, 1507.80  $\rightarrow$  347.16 and TIC), compound obtained by UPLC–ESI–MS–MS in the positive ion mode for crude extract solution in *C. hirsuta*.



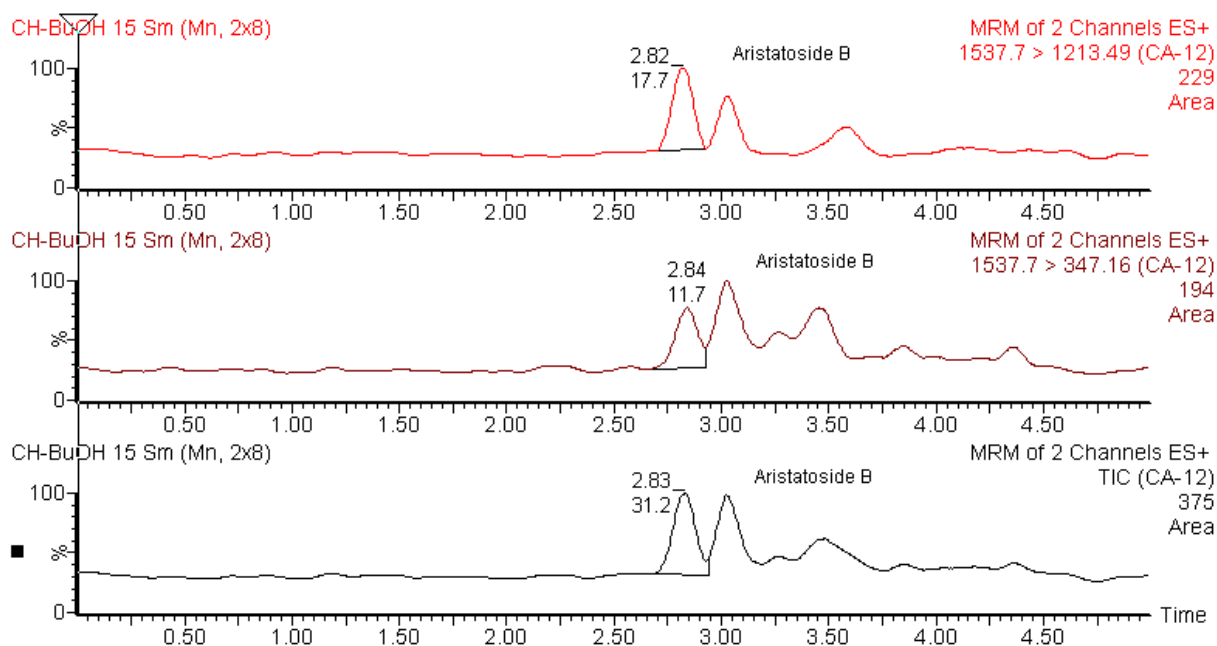
**S 5.** Chromatograms of Gazipashoside A ( $m/z$ : 1375.46  $\rightarrow$  1051.55, 1375.46  $\rightarrow$  347.19 and TIC), compound obtained by UPLC-ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



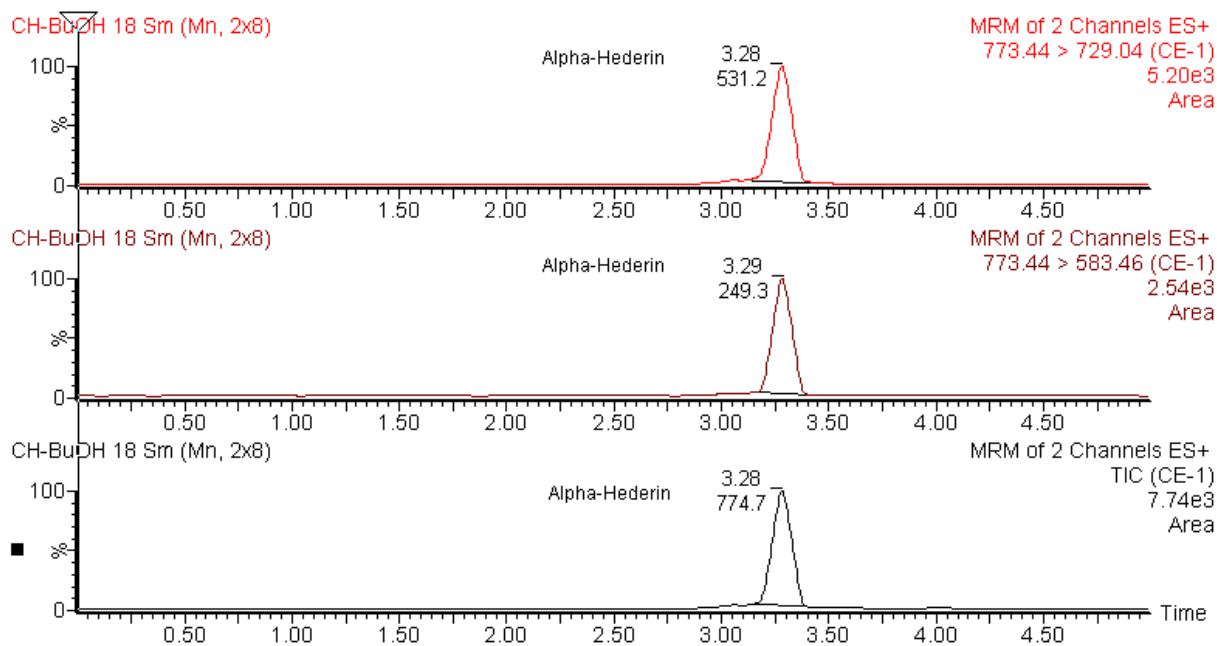
**S 6.** Chromatograms of Aristatoside C ( $m/z$ : 1200.09  $\rightarrow$  1156.12, 1200.09  $\rightarrow$  595.15 and TIC), compound obtained by UPLC-ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



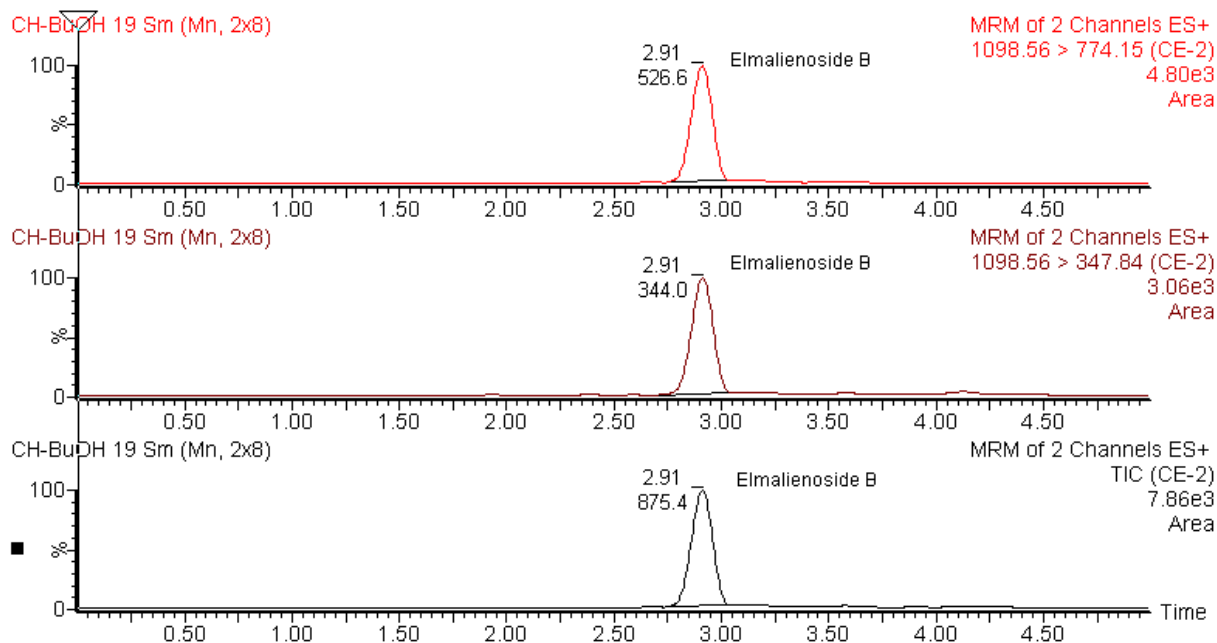
**S 7.** Chromatograms of Aristatoside A ( $m/z$ : 1567.70  $\rightarrow$  639.13, 1567.7  $\rightarrow$  347.19 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



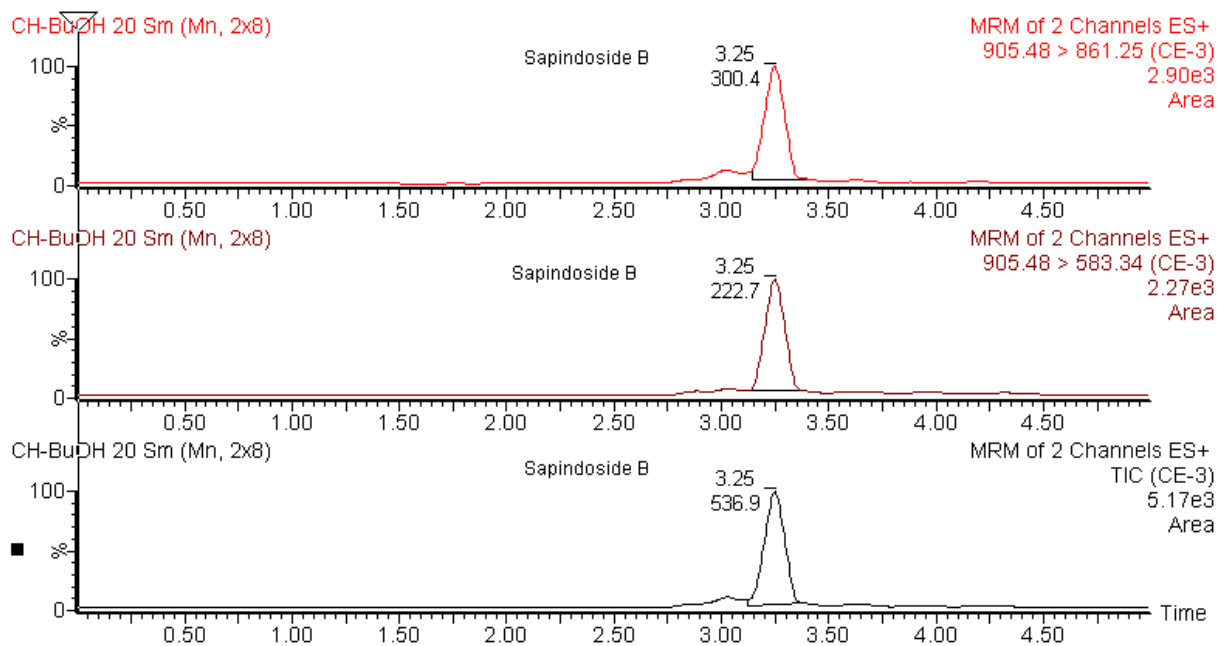
**S 8.** Chromatograms of Aristatoside B ( $m/z$ : 1537.70  $\rightarrow$  1213.49, 1537.70  $\rightarrow$  347.16 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



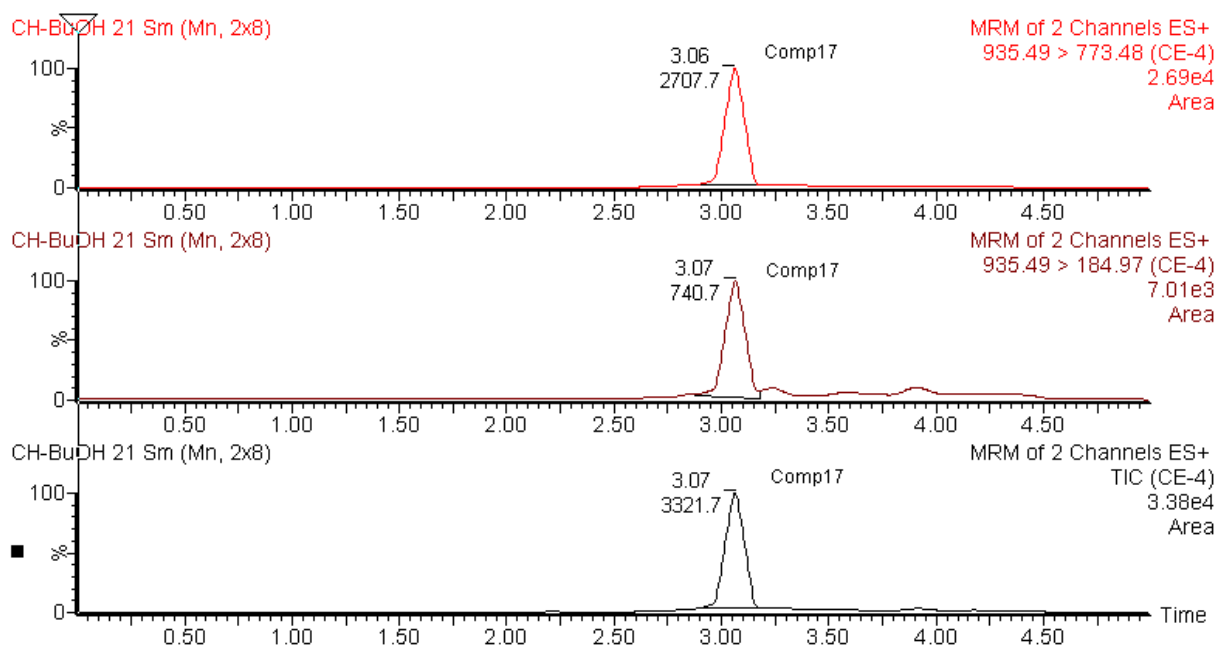
**S 9.** Chromatograms of  $\alpha$ -Hederin ( $m/z$ : 773.44  $\rightarrow$  729.04, 773.44  $\rightarrow$  583.46 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



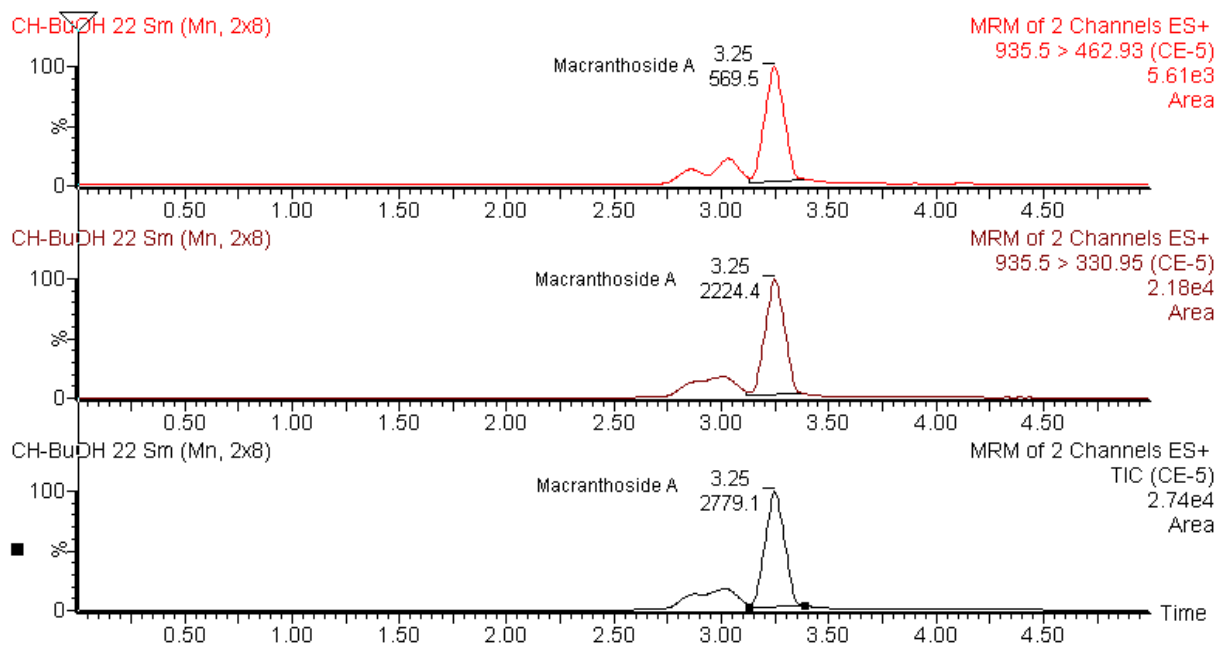
**S 10.** Chromatograms of Elmalienoside B ( $m/z$ : 1098.56  $\rightarrow$  774.15, 1098.56  $\rightarrow$  347.84 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



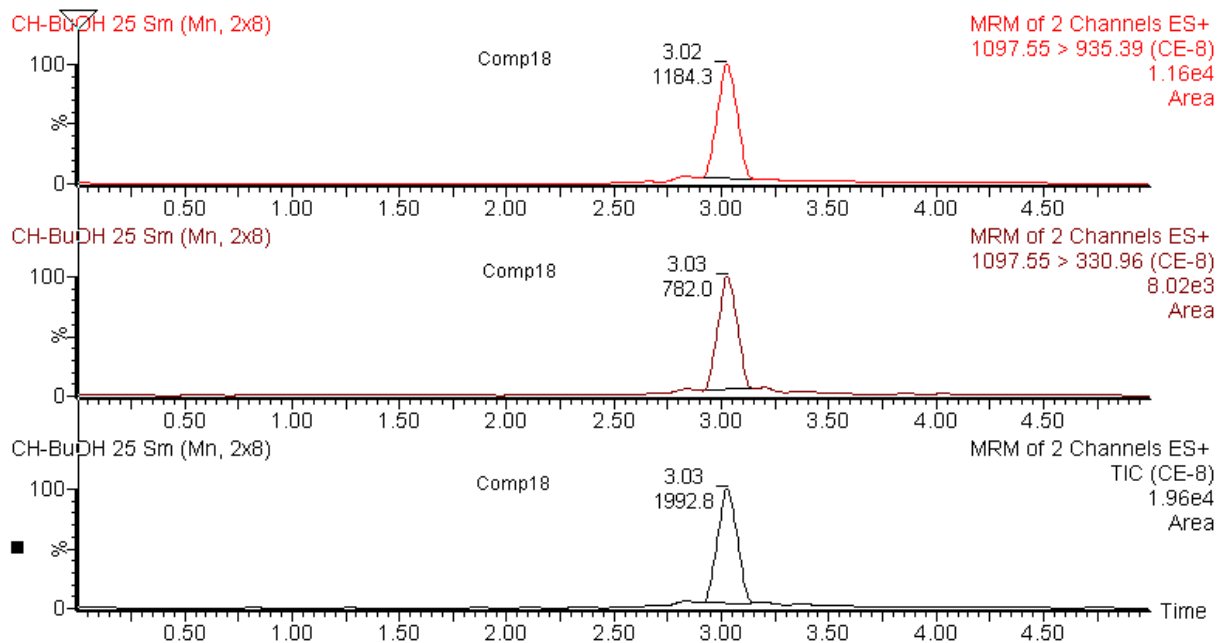
**S 11.** Chromatograms of Sapindoside B ( $m/z$ : 905.48  $\rightarrow$  861.25, 905.48  $\rightarrow$  583.34 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



**S 12.** Chromatograms of 3-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -L-arabinopyranosyl hederagenin 28-O- $\beta$ -D-glucopyranosyl ester ( $m/z$ : 935.49  $\rightarrow$  773.48, 935.49  $\rightarrow$  184.97 and TIC), compound obtained UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.

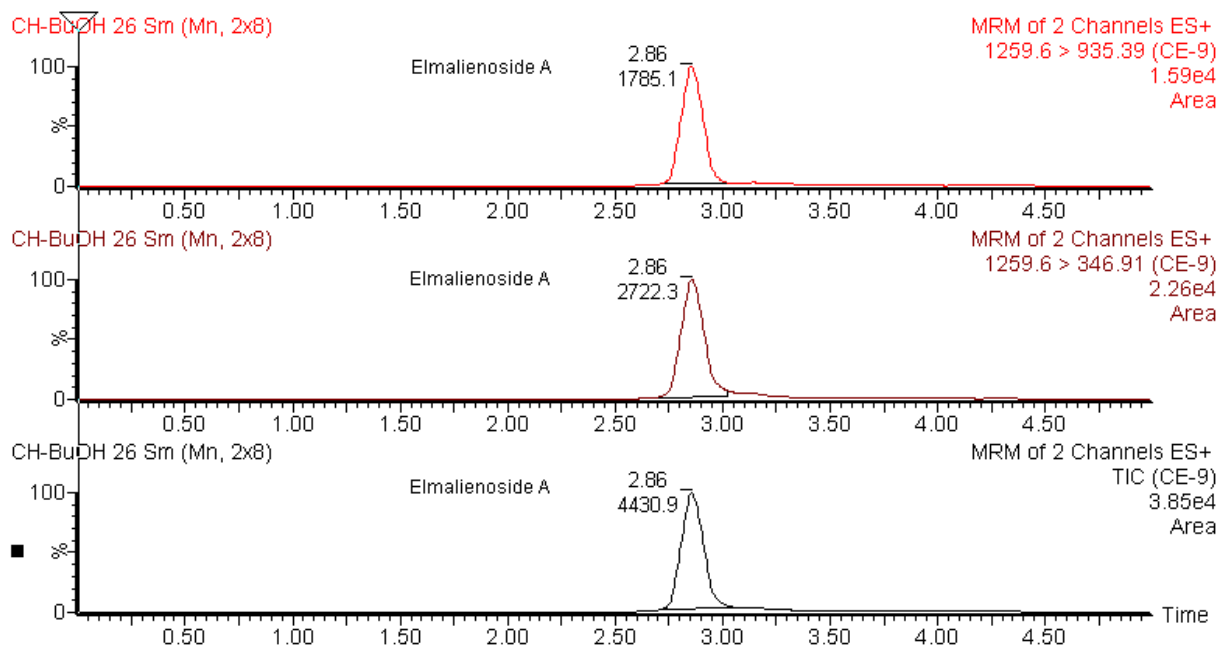


**S 13.** Chromatograms of Macranthoside A ( $m/z$ : 935.50  $\rightarrow$  462.93, 935.50  $\rightarrow$  330.95 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.

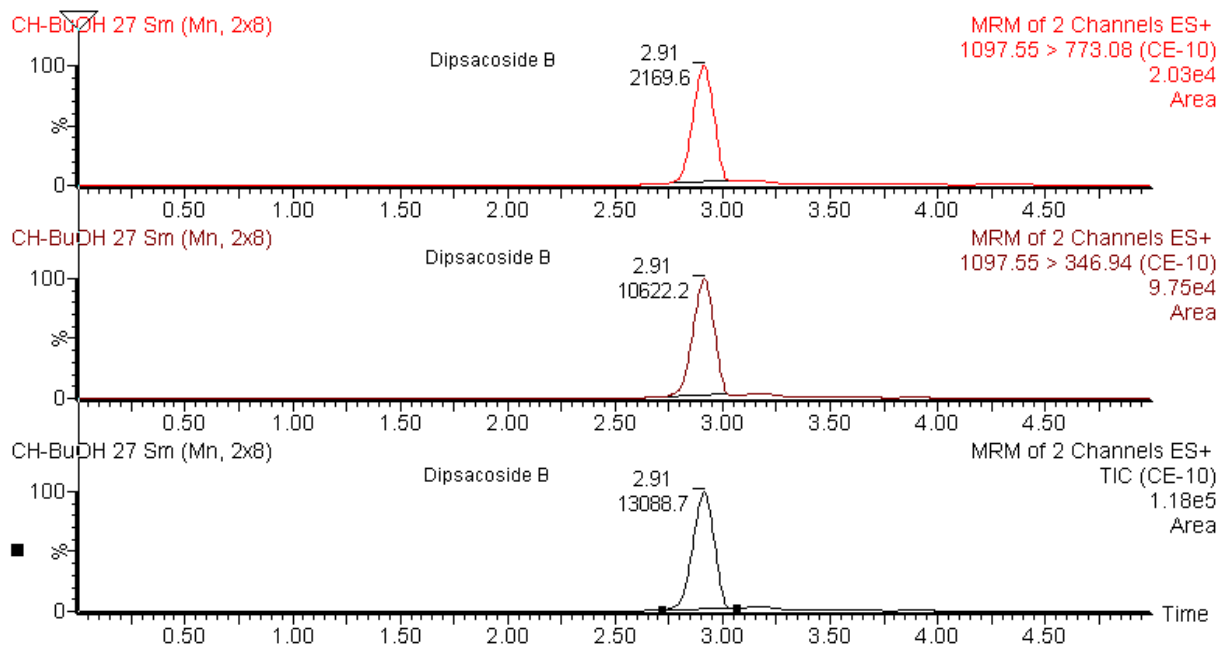


**S 14.** Chromatograms of 3-O-β-D-glucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl hederagenin 28-O-β-D-glucopyranosyl ester ( $m/z$ : 1097.55  $\rightarrow$  935.39, 1097.55  $\rightarrow$  330.96 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.

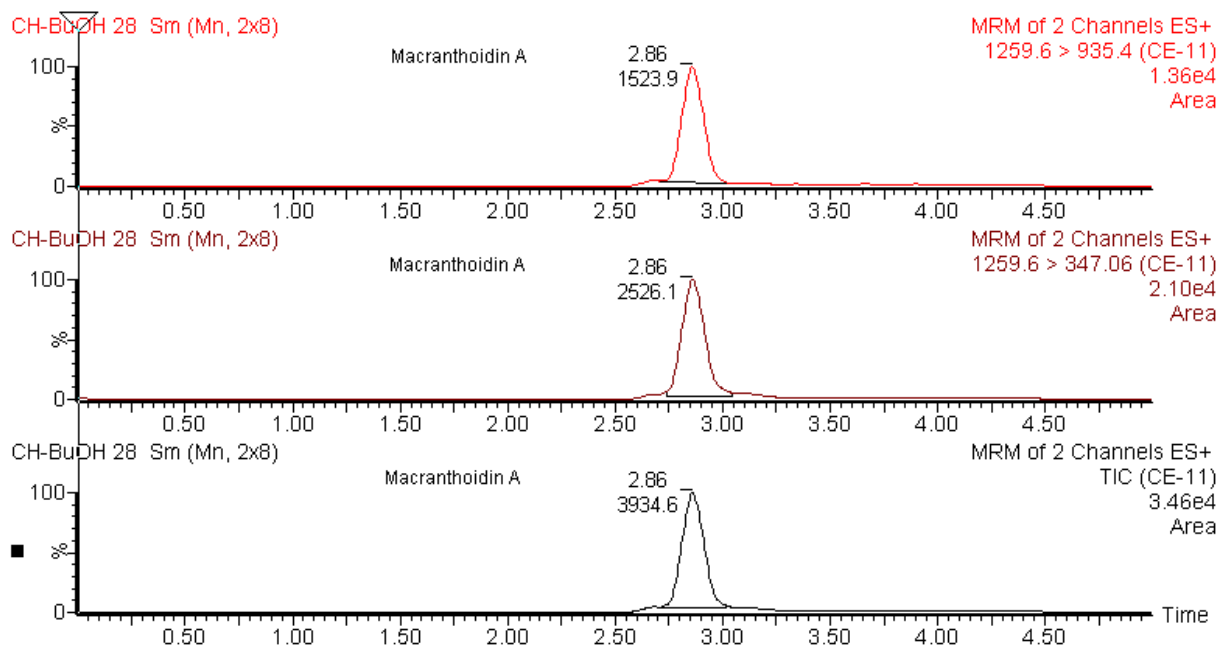




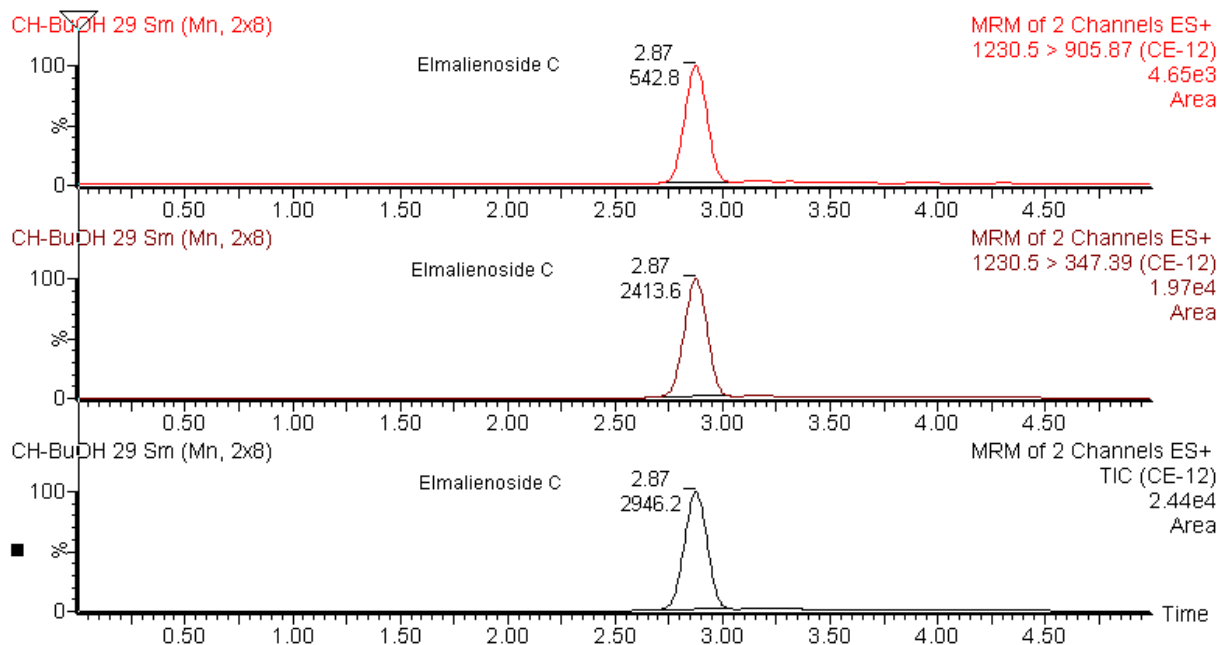
**S 15.** Chromatograms of Elmalienoside A ( $m/z$ : 1259.6  $\rightarrow$  935.39, 1259.60  $\rightarrow$  346.91 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



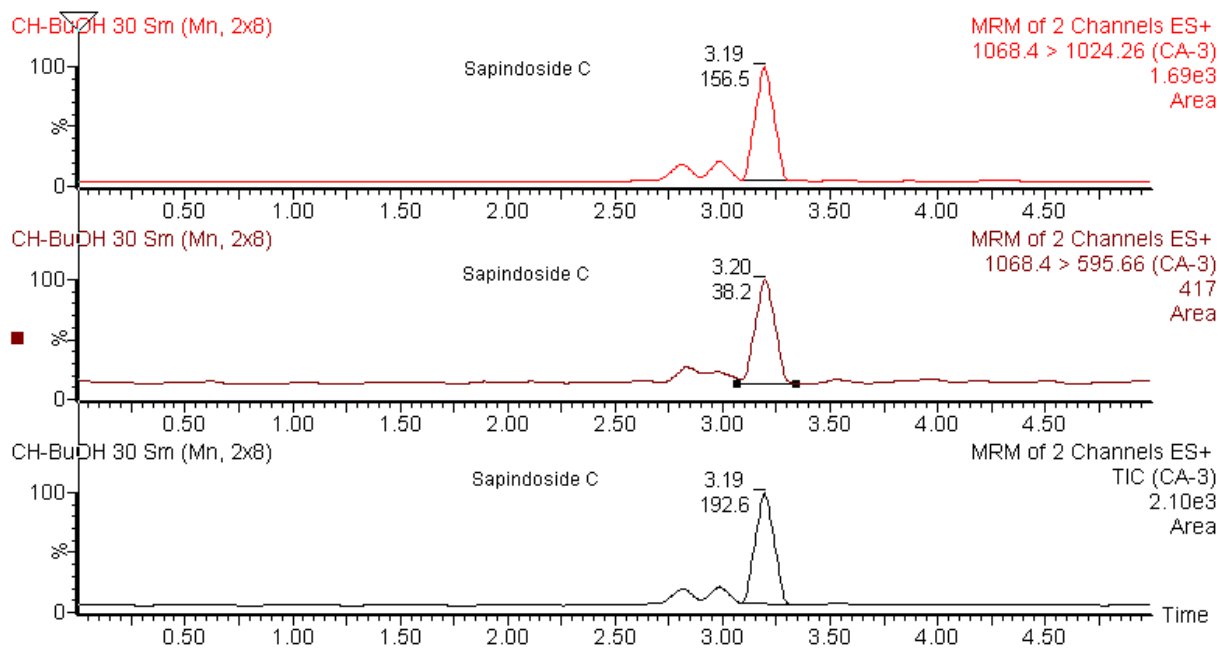
**S 16.** Chromatograms of Dipsacoside B ( $m/z$ : 1097.55  $\rightarrow$  773.08, 1097.55  $\rightarrow$  346.94 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



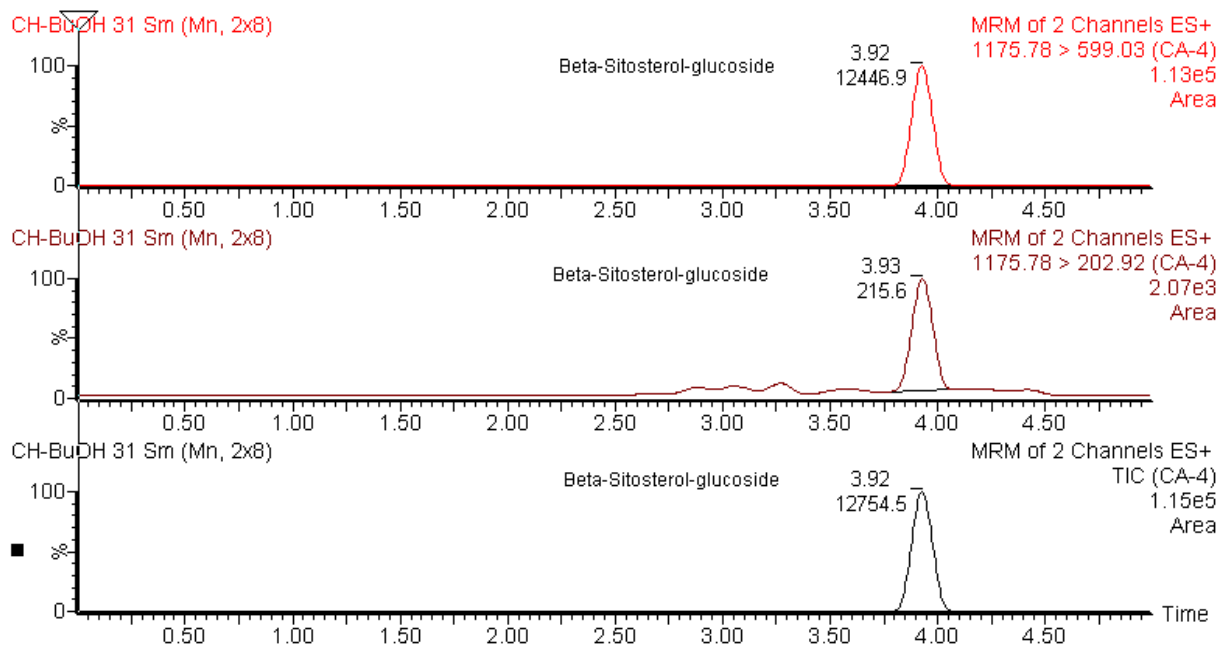
**S 17.** Chromatograms of Macranthoidin A ( $m/z$ : 1259.60  $\rightarrow$  935.40, 1259.60  $\rightarrow$  347.06 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



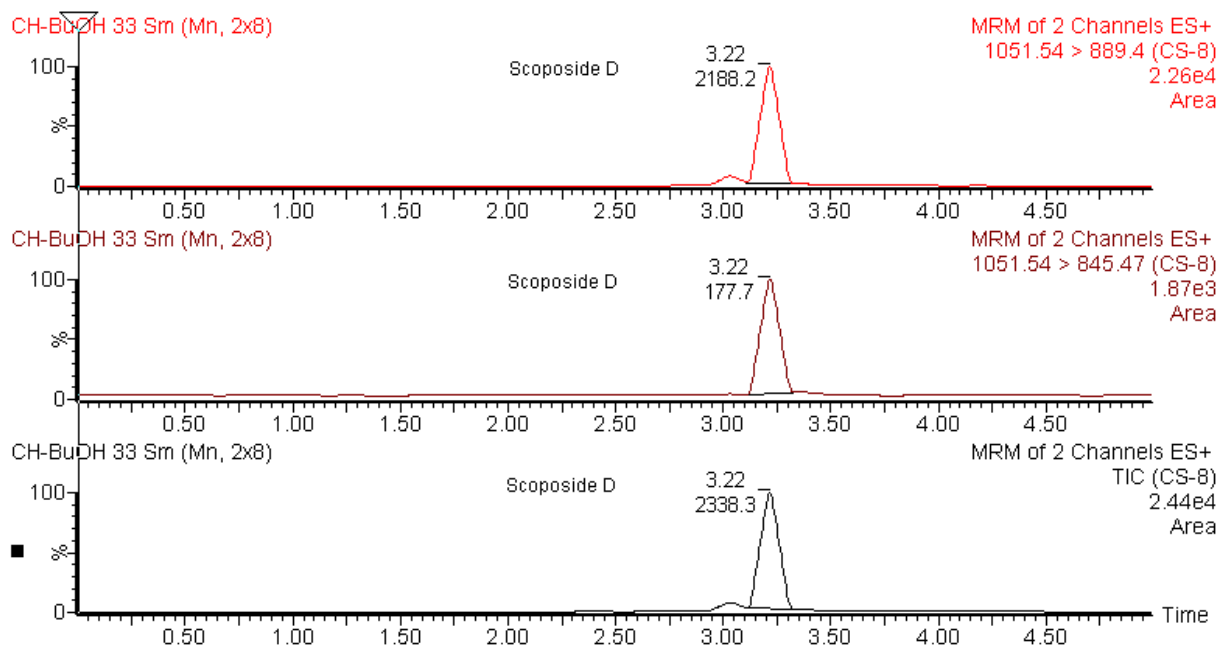
**S 18.** Chromatograms of Elmalienoside C ( $m/z$ : 1230.50  $\rightarrow$  905.87, 1230.50  $\rightarrow$  347.39 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



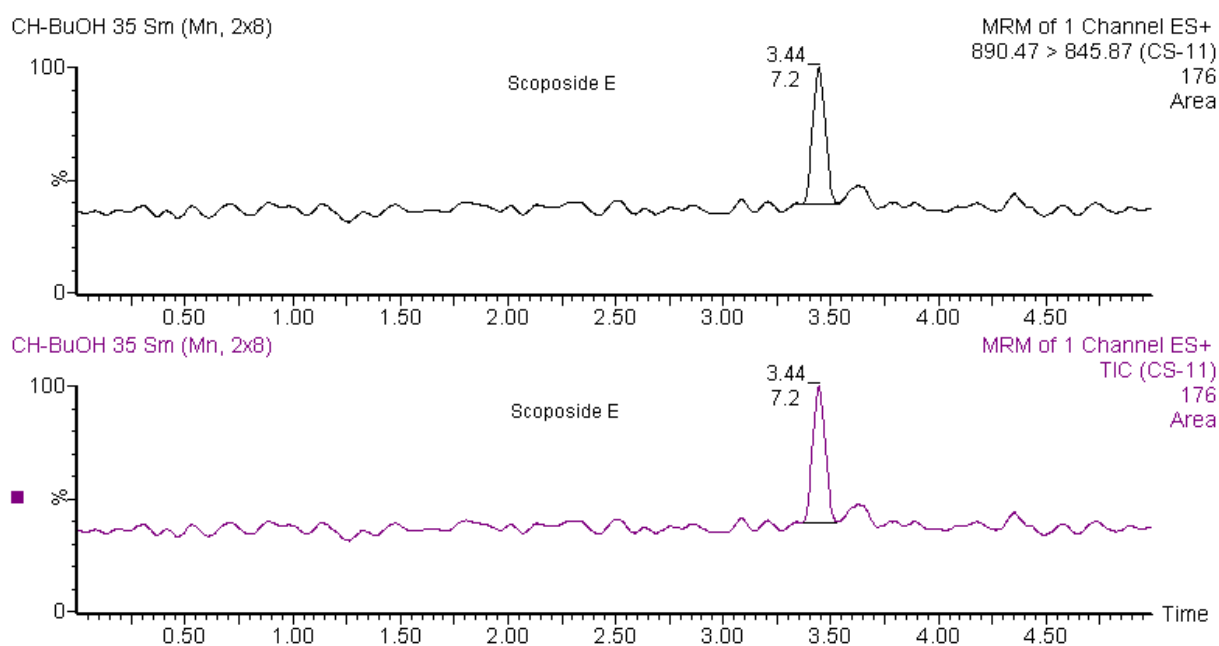
**S 19.** Chromatograms of Sapindoside C ( $m/z$ : 1068.40  $\rightarrow$  1024.26, 1068.40  $\rightarrow$  595.66 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



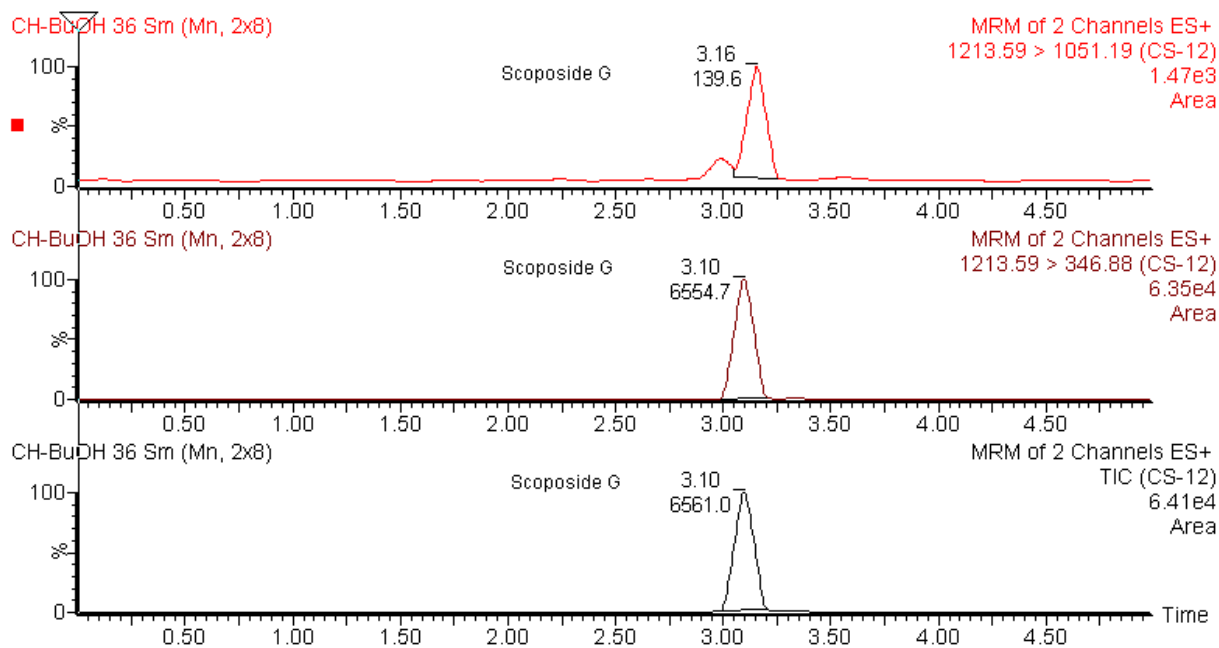
**S 20.** Chromatograms of  $\beta$ -Sitosterol-Glucoside ( $m/z$ : 1175.78  $\rightarrow$  599.03, 1175.78  $\rightarrow$  202.92 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*



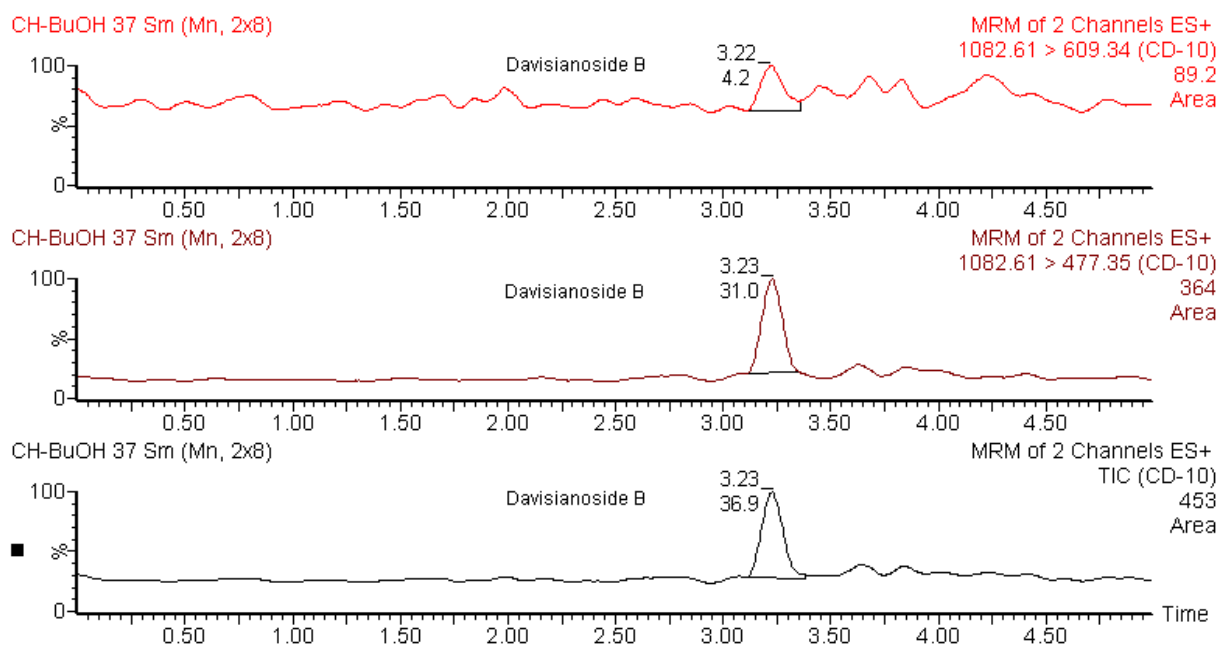
S 21. Chromatograms of Scoposide D ( $m/z$ : 1051.54  $\rightarrow$  889.40, 1051.54  $\rightarrow$  845.47 and TIC), compound obtained by UPLC-ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



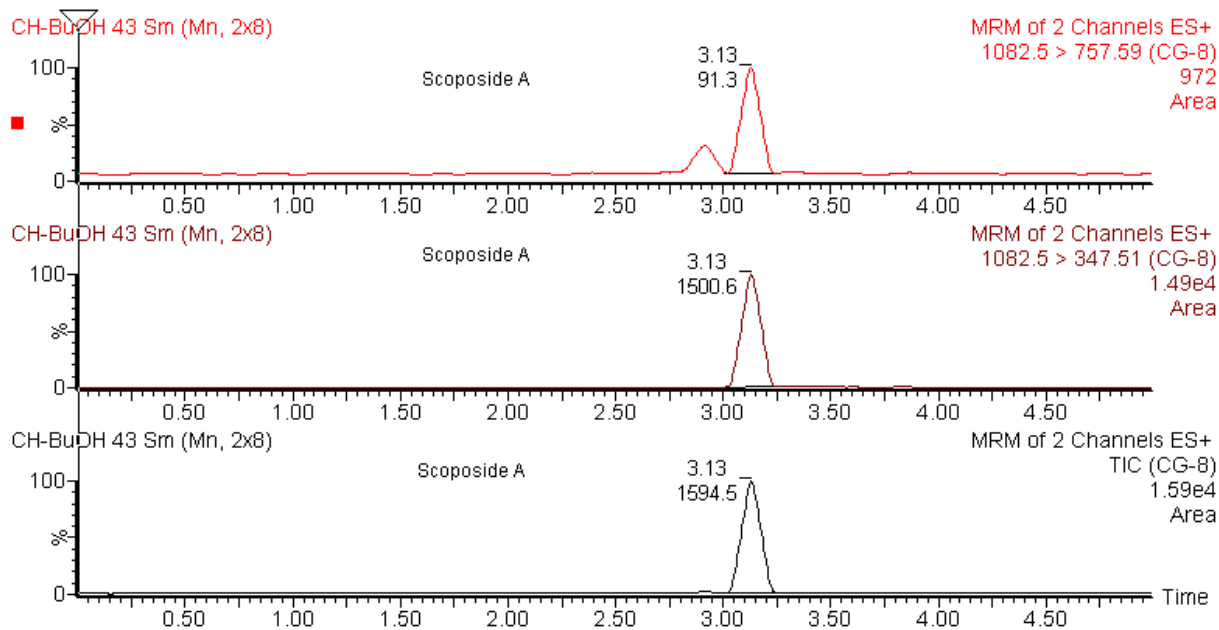
S 22. Chromatograms of Scoposide E ( $m/z$ : 890.47  $\rightarrow$  845.87 and TIC), compound obtained by UPLC-ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



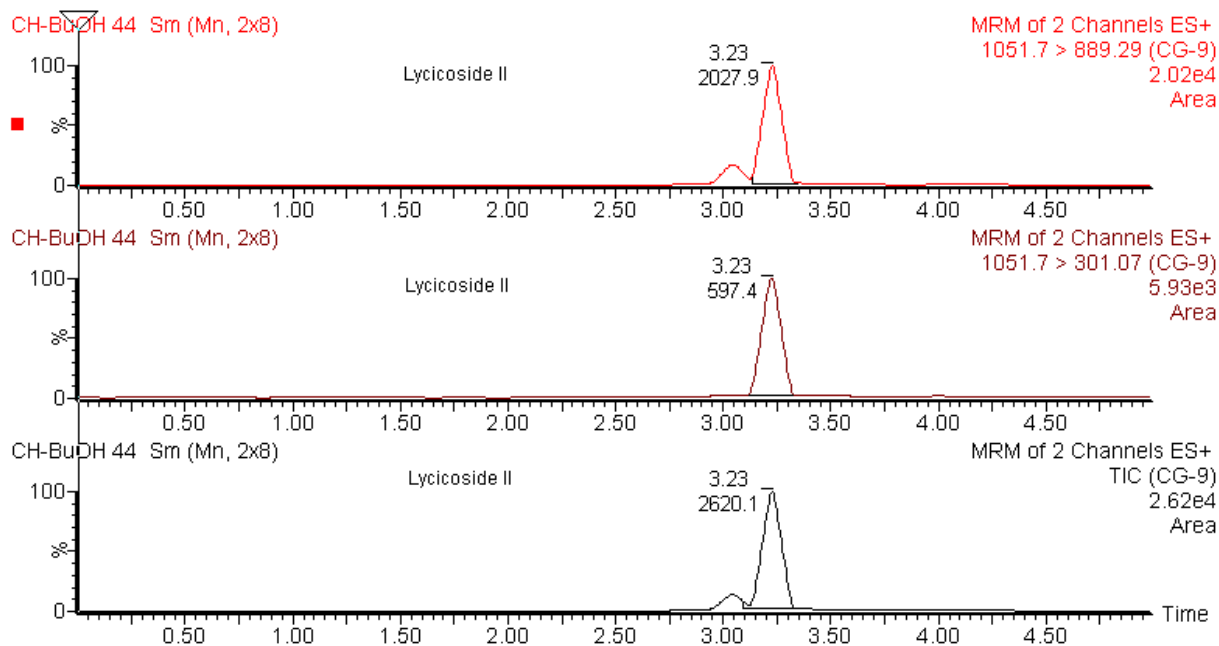
**S 23.** Chromatograms of Scoposide G ( $m/z$ : 1213.59  $\rightarrow$  1051.19, 1213.59  $\rightarrow$  346.88 and TIC), compound obtained by UPLC-ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



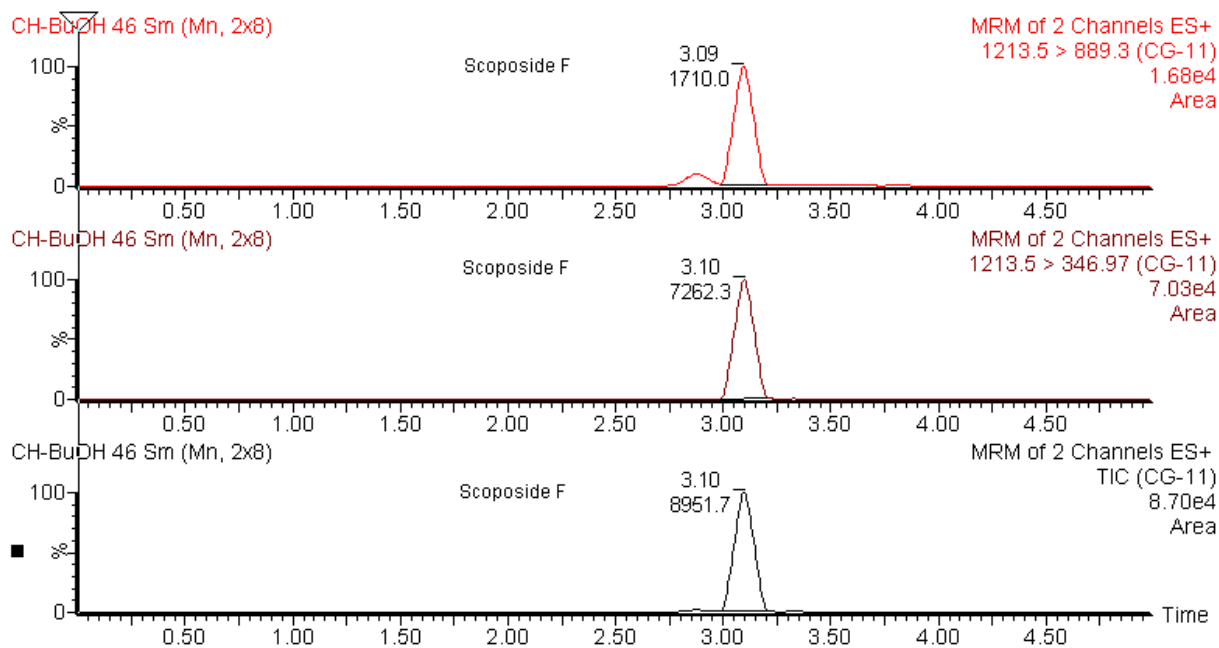
**S 24.** Chromatograms of Davisianoside B ( $m/z$ : 1082.61  $\rightarrow$  609.34, 1082.61  $\rightarrow$  477.35 and TIC), compound obtained by UPLC-ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



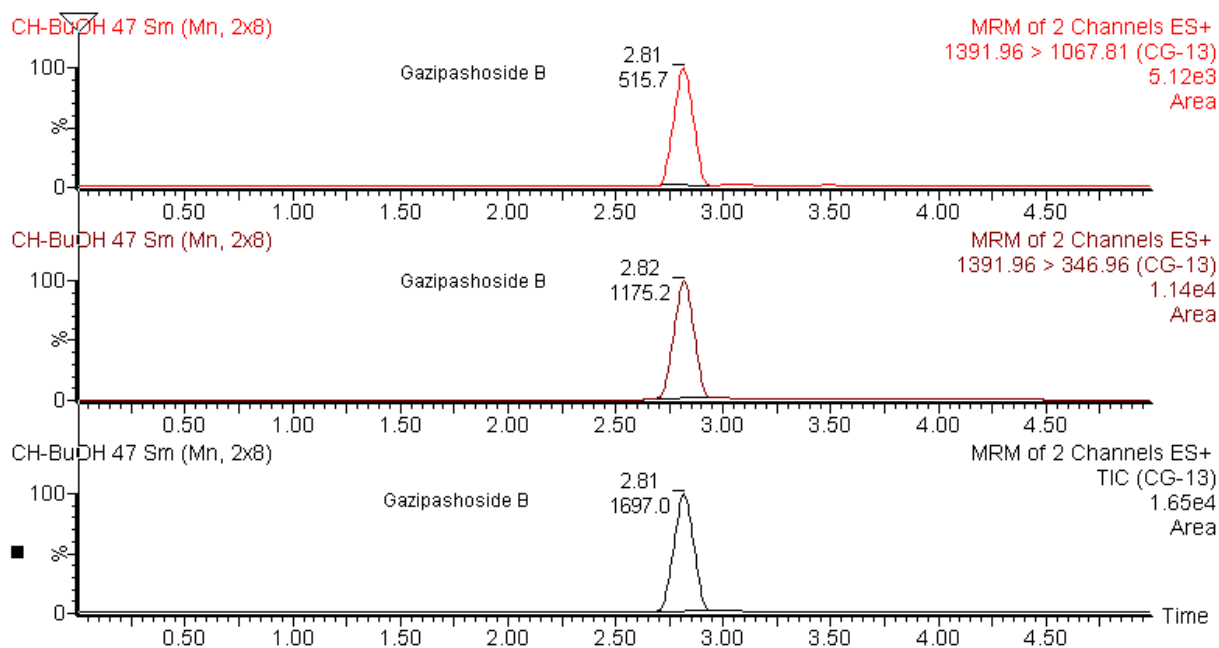
**S 25.** Chromatograms of Scoposide A ( $m/z$ : 1082.50  $\rightarrow$  757.59, 1082.50  $\rightarrow$  347.51 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



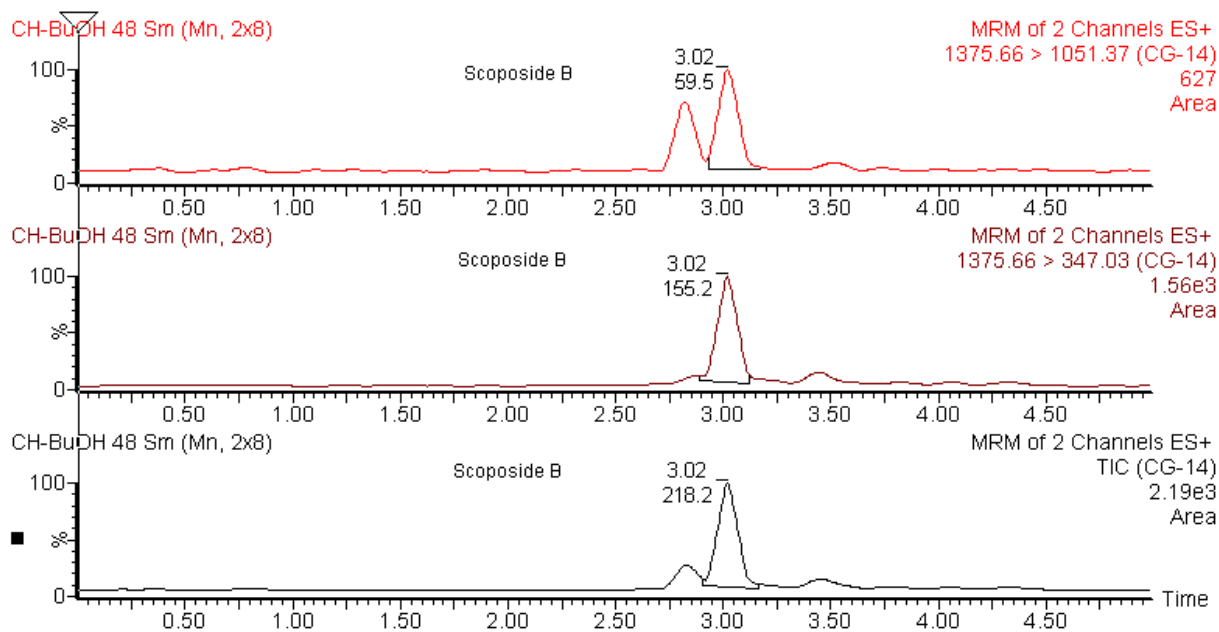
**S 26.** Chromatograms of Lycicoside II ( $m/z$ : 1051.70  $\rightarrow$  889.29, 1051.70  $\rightarrow$  301.07 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



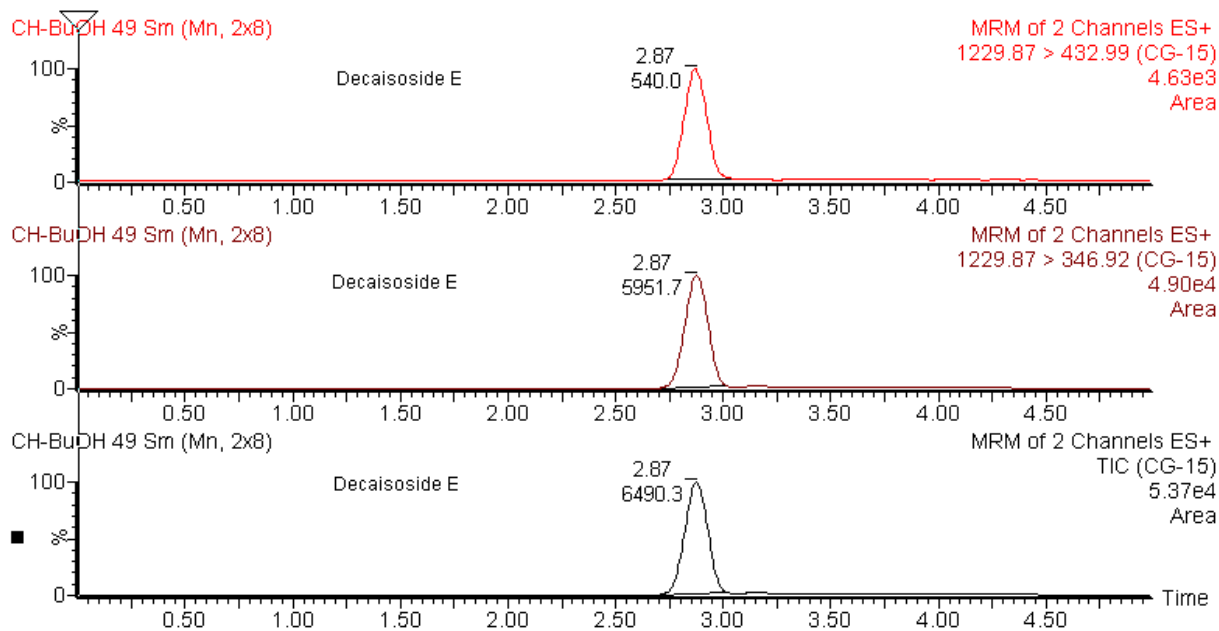
**S 27.** Chromatograms of Scoposide F ( $m/z$ : 1213.50  $\rightarrow$  889.30, 1213.50  $\rightarrow$  346.97 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.



**S 28.** Chromatograms of Gazipashoside B ( $m/z$ : 1391.96  $\rightarrow$  1067.81, 1391.96  $\rightarrow$  346.96 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.

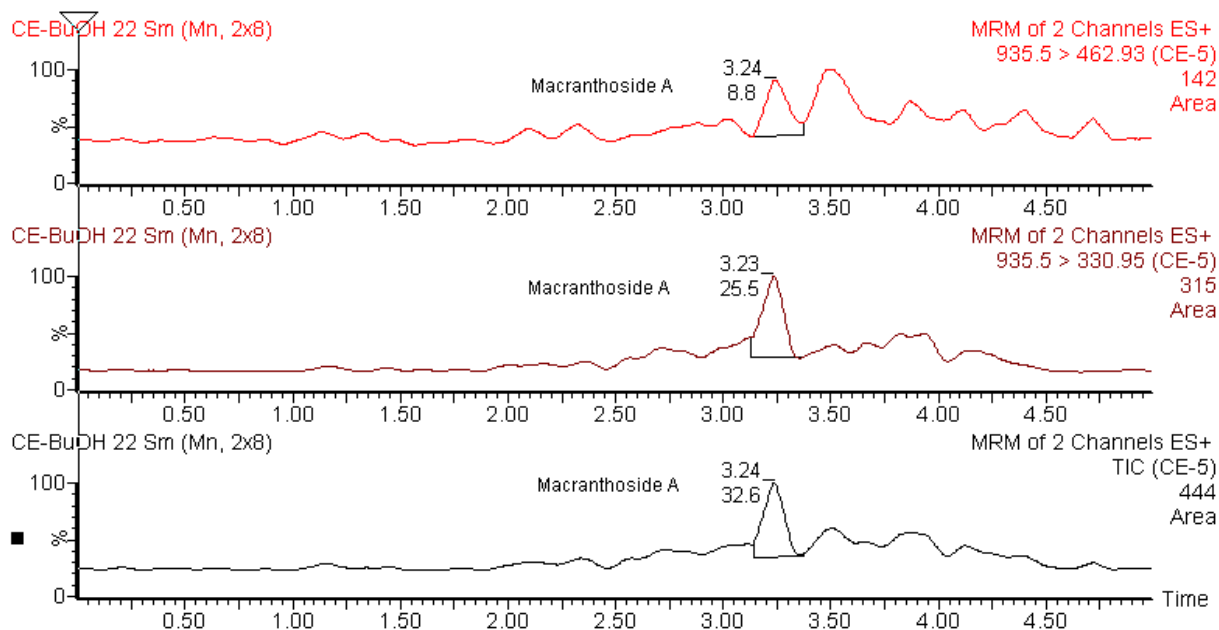


**S 29.** Chromatograms of Scoposide B ( $m/z$ : 1375.66  $\rightarrow$  1051.37, 1375.66  $\rightarrow$  347.03 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.

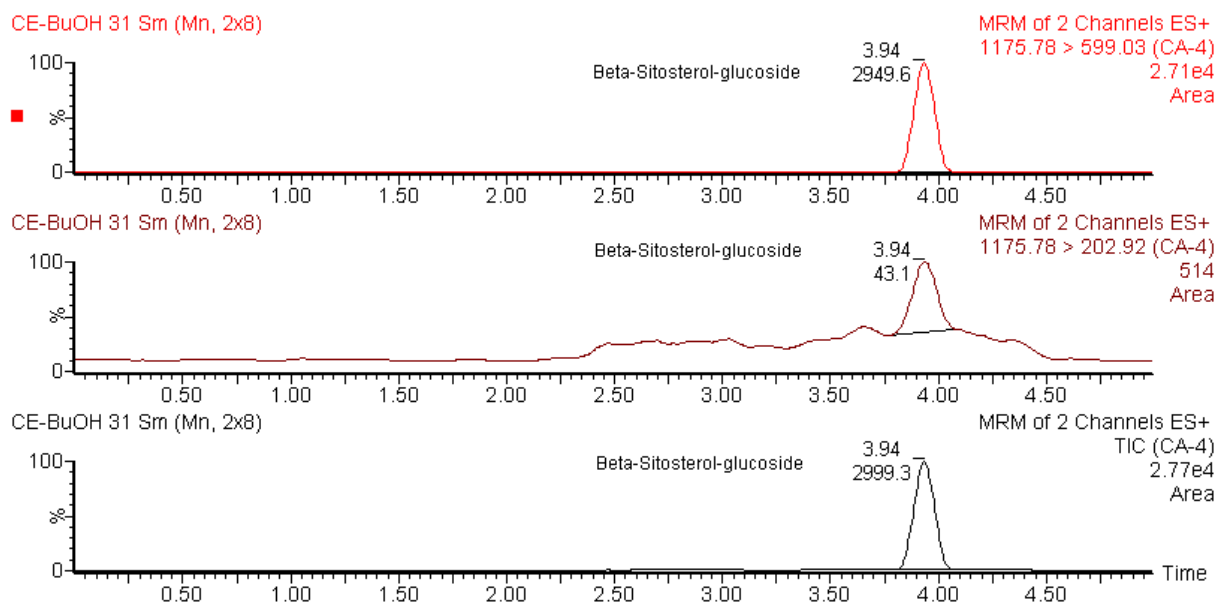


**S 30.** Chromatograms of Decaisoside E ( $m/z$ : 1229.87  $\rightarrow$  432.99, 1229.87  $\rightarrow$  346.92 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. hirsuta*.

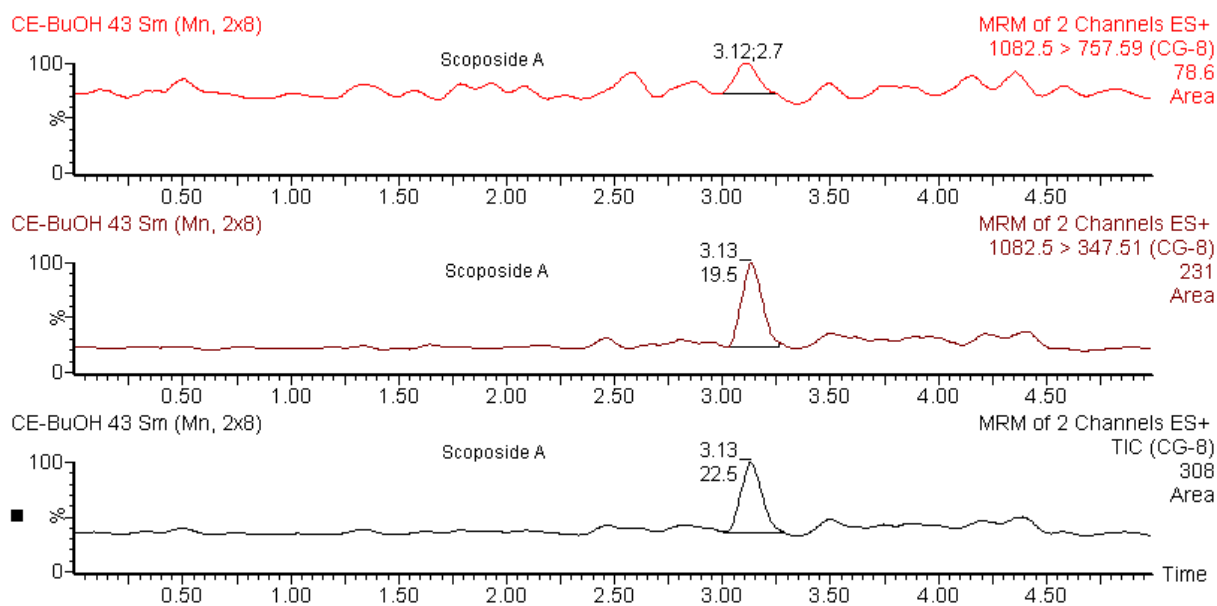




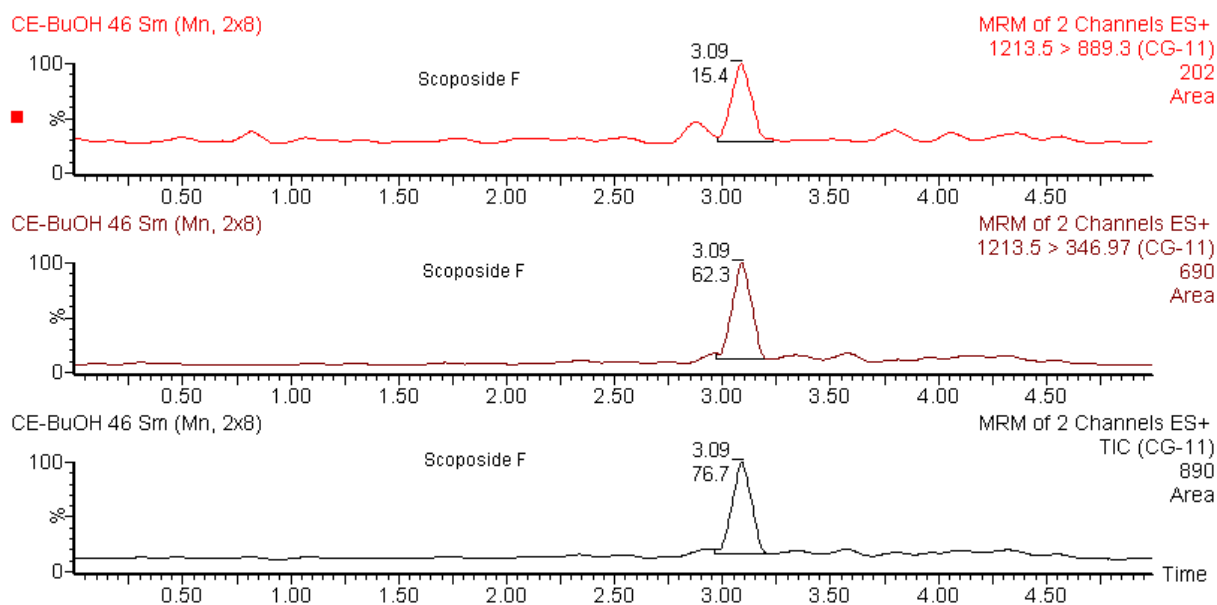
**S 31.** Chromatograms of Macranthoside A ( $m/z$ : 935.50  $\rightarrow$  462.93, 935.50  $\rightarrow$  330.95 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. elazigensis* var. *elazigensis*.



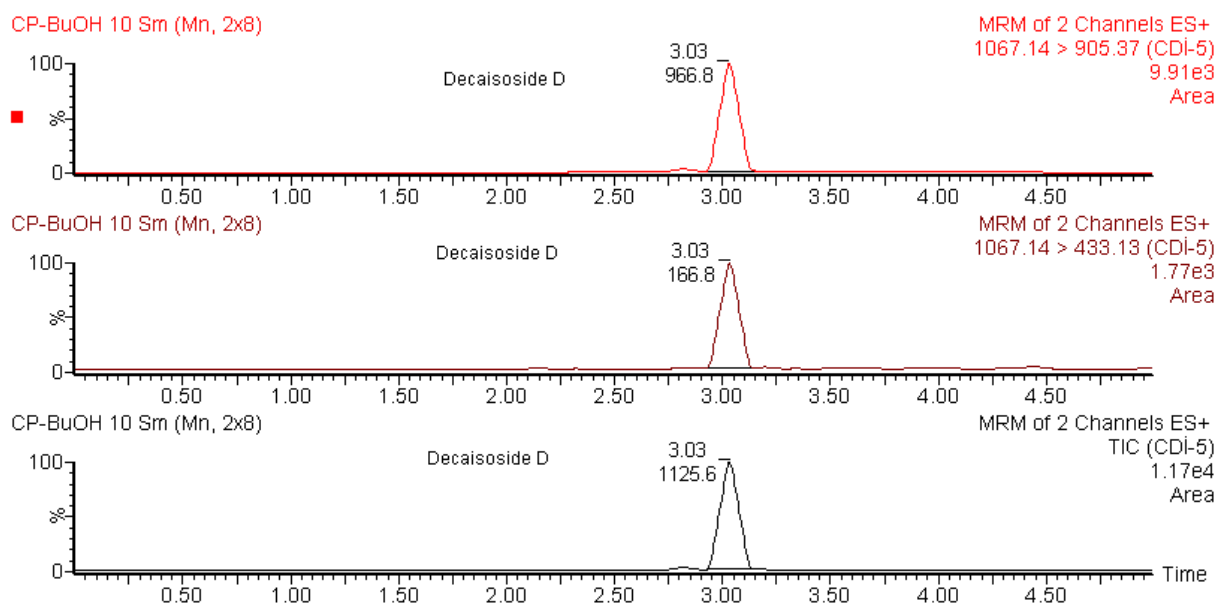
**S 32.** Chromatograms of  $\beta$ -Sitosterol-Glucoside ( $m/z$ : 1175.78  $\rightarrow$  599.03, 1175.78  $\rightarrow$  202.92 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. elazigensis* var. *elazigensis*.



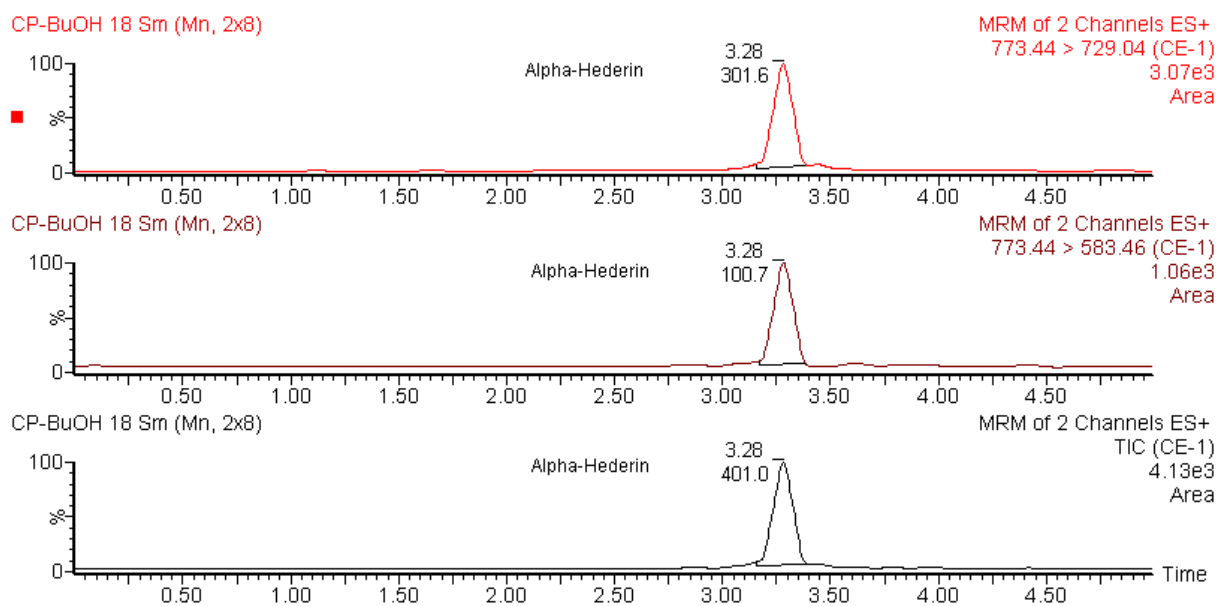
**S 33.** Chromatograms of Scoposide A ( $m/z$ : 1082.50  $\rightarrow$  757.59, 1082.50  $\rightarrow$  347.51 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. elazigensis* var. *elazigensis*.



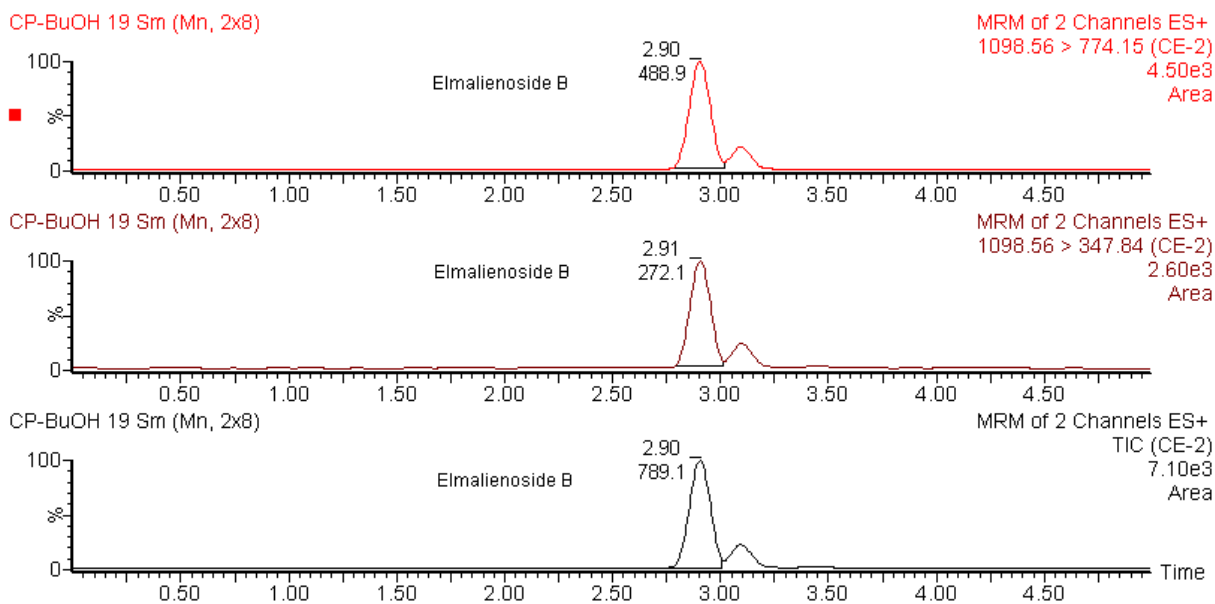
**S 34.** Chromatograms of Scoposide F ( $m/z$ : 1213.50  $\rightarrow$  889.30, 1213.50  $\rightarrow$  346.97 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. elazigensis* var. *elazigensis*.



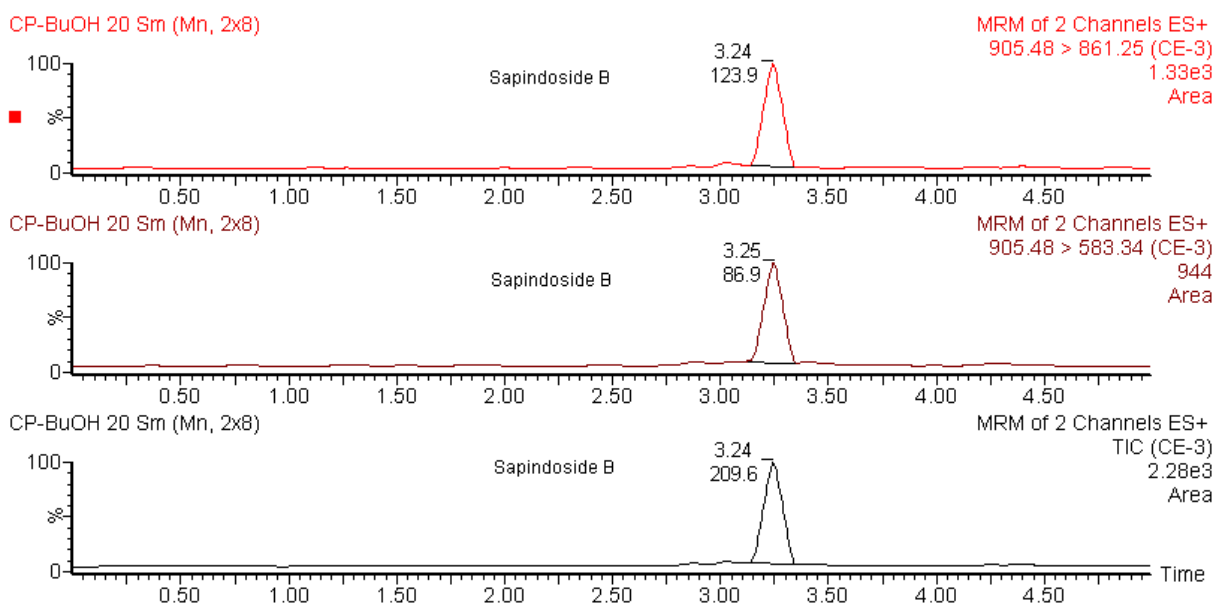
**S 35.** Chromatograms of Decaisoside D ( $m/z$ : 1067.14  $\rightarrow$  905.37, 1067.14  $\rightarrow$  433.13 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



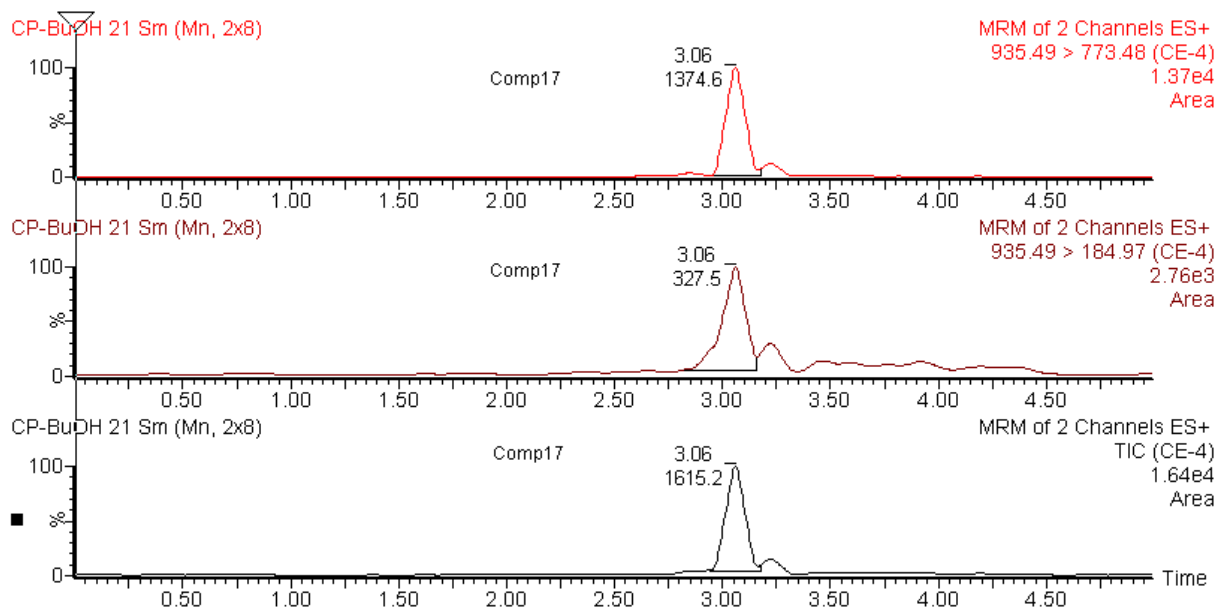
**S 36.** Chromatograms of  $\alpha$ -Hederin ( $m/z$ : 773.44  $\rightarrow$  729.04, 773.44  $\rightarrow$  583.46 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



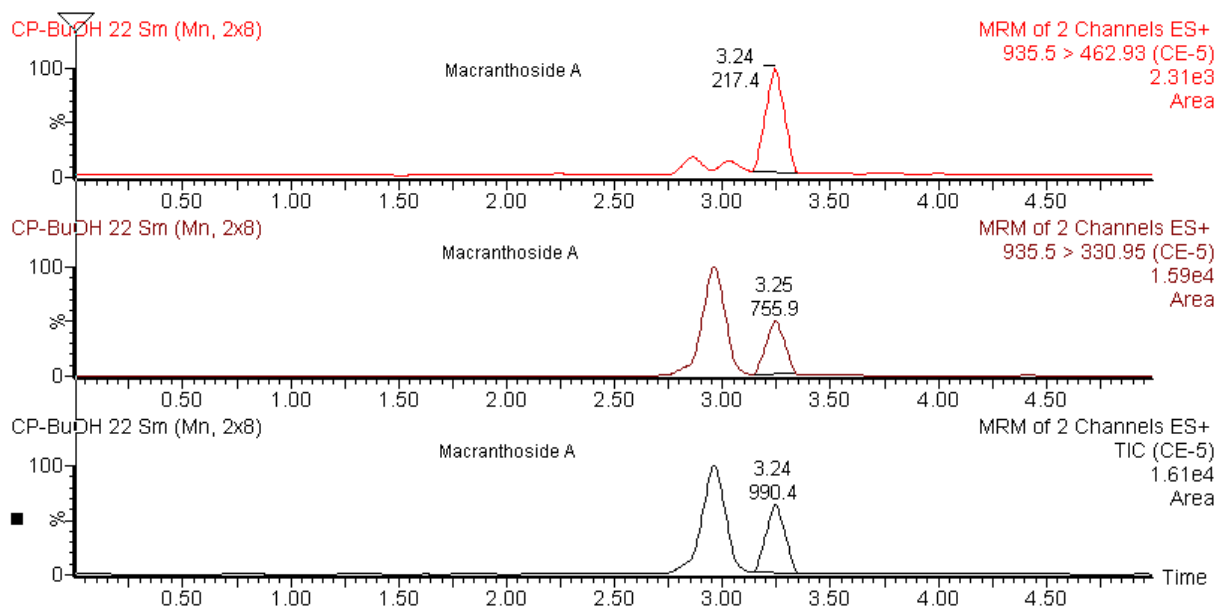
**S 37.** Chromatograms of Elmalienoside B ( $m/z$ : 1098.56  $\rightarrow$  774.15, 1098.56  $\rightarrow$  347.84 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



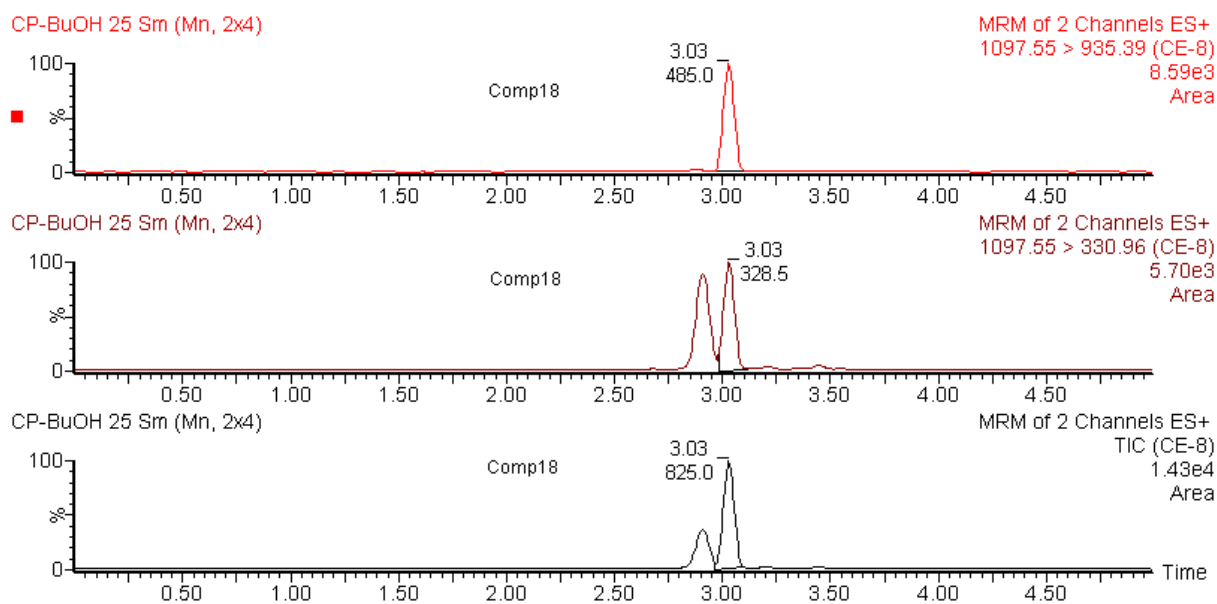
**S 38.** Chromatograms of Sapindoside B ( $m/z$ : 905.48  $\rightarrow$  861.25, 905.48  $\rightarrow$  583.34 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



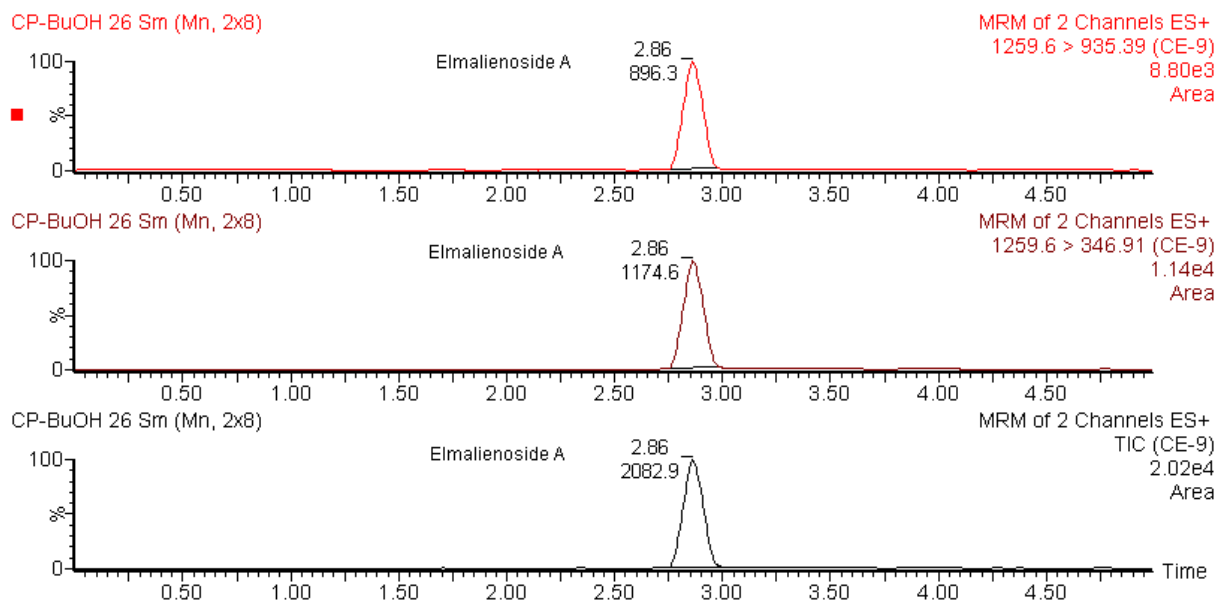
**S 39.** Chromatograms of 3-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -L-arabinopyranosyl hederagenin 28-O- $\beta$ -D-glucopyranosyl ester ( $m/z$ : 935.49  $\rightarrow$  773.48, 935.49  $\rightarrow$  184.97 and TIC), compound obtained by UPLC-ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



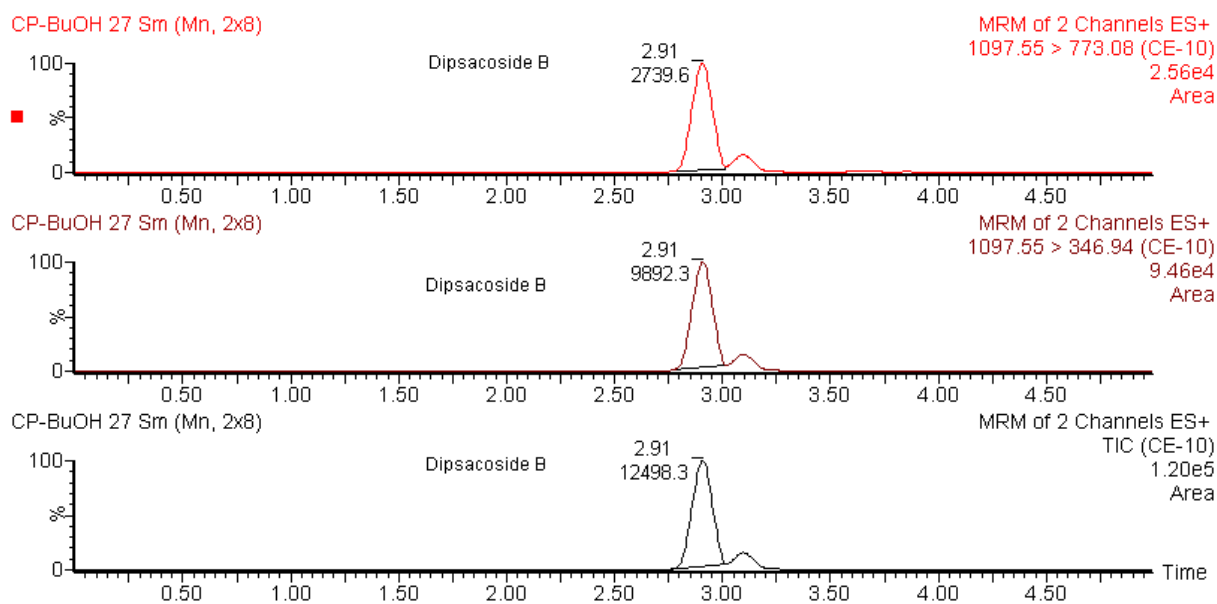
**S 40.** Chromatograms of Macranthoside A ( $m/z$ : 935.50  $\rightarrow$  462.93, 935.50  $\rightarrow$  330.95 and TIC), compound obtained by UPLC-ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



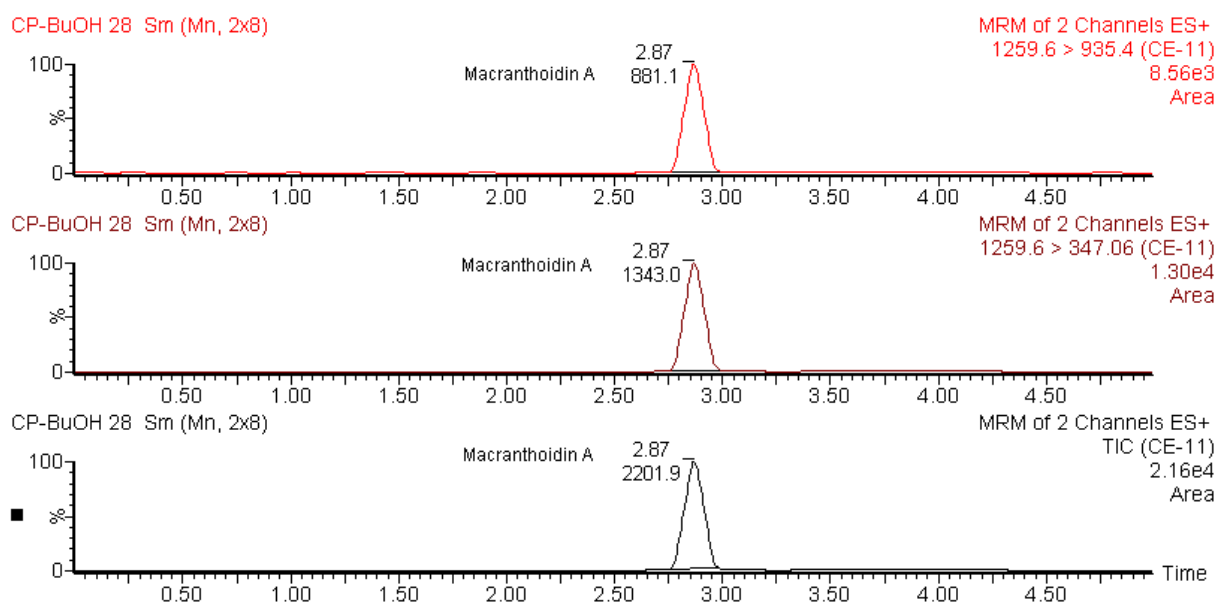
**S 41.** Chromatograms of 3-O- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3)- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -L-arabinopyranosyl hederagenin 28-O- $\beta$ -D-glucopyranosyl ester ( $m/z$ : 1097.55  $\rightarrow$  935.39, 1097.55  $\rightarrow$  330.96 and TIC), compound obtained by UPLC-ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



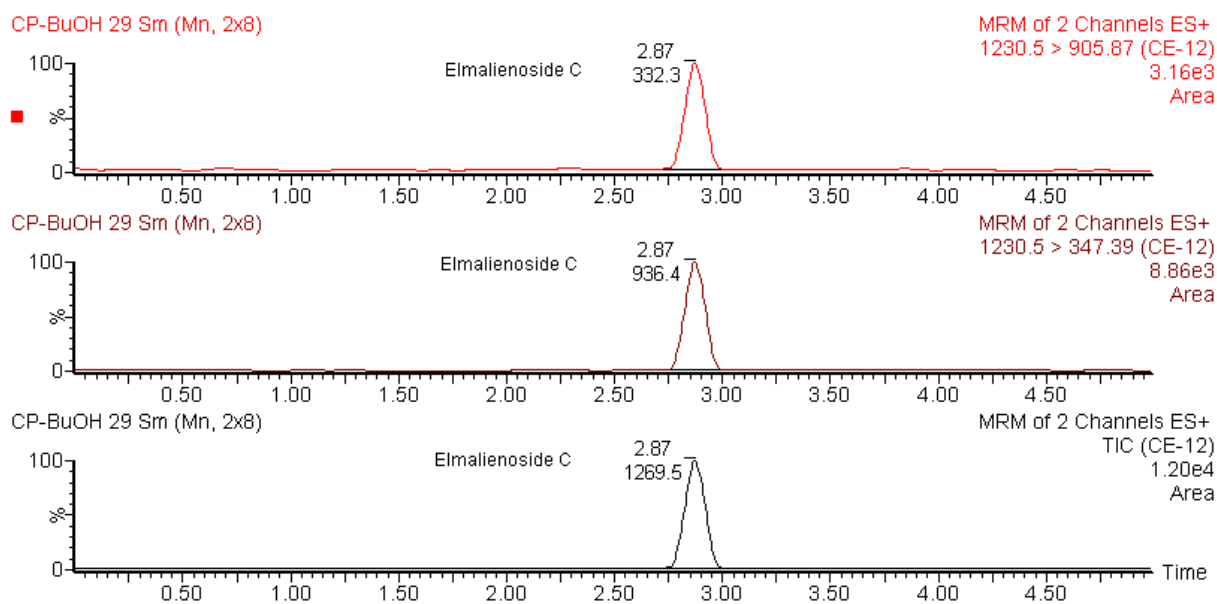
**S 42.** Chromatograms of Elmalienoside A ( $m/z$ : 1259.60  $\rightarrow$  935.39, 1259.60  $\rightarrow$  346.91 and TIC), compound obtained by UPLC-ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*



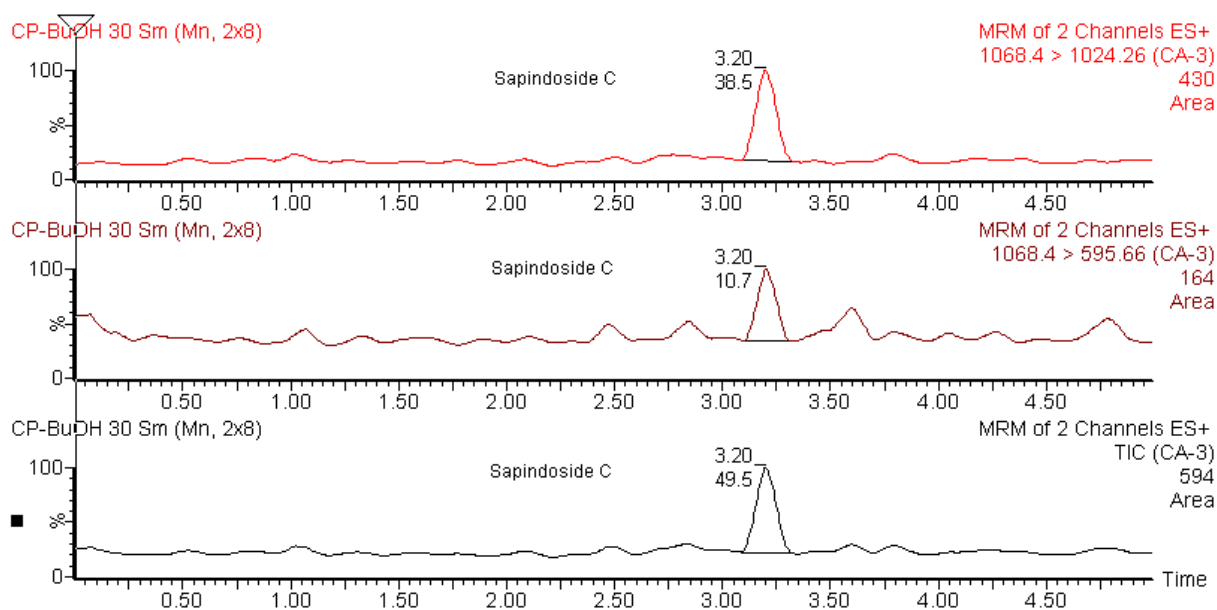
**S 43.** Chromatograms of Dipsacoside B ( $m/z$ : 1097.55  $\rightarrow$  773.08, 1097.55  $\rightarrow$  346.94 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



**S 44.** Chromatograms of Macranthoidin A ( $m/z$ : 1259.60  $\rightarrow$  935.40, 1259.60  $\rightarrow$  347.06 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.

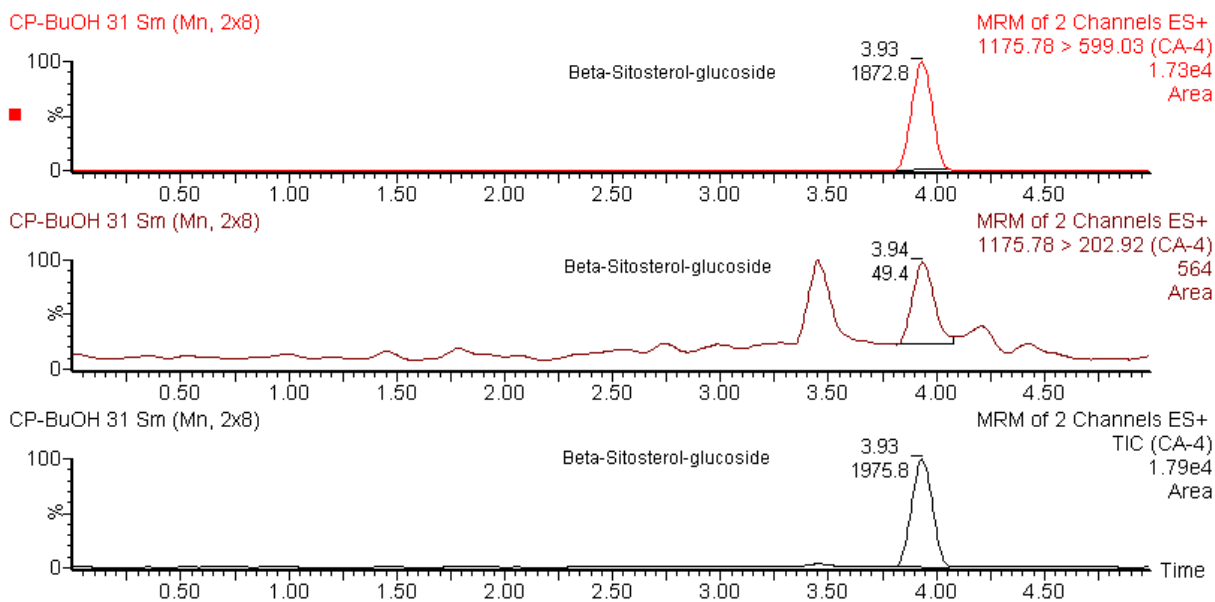


**S 45.** Chromatograms of Elmalienoside C ( $m/z$ : 1230.50  $\rightarrow$  905.87, 1230.50  $\rightarrow$  347.39 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.

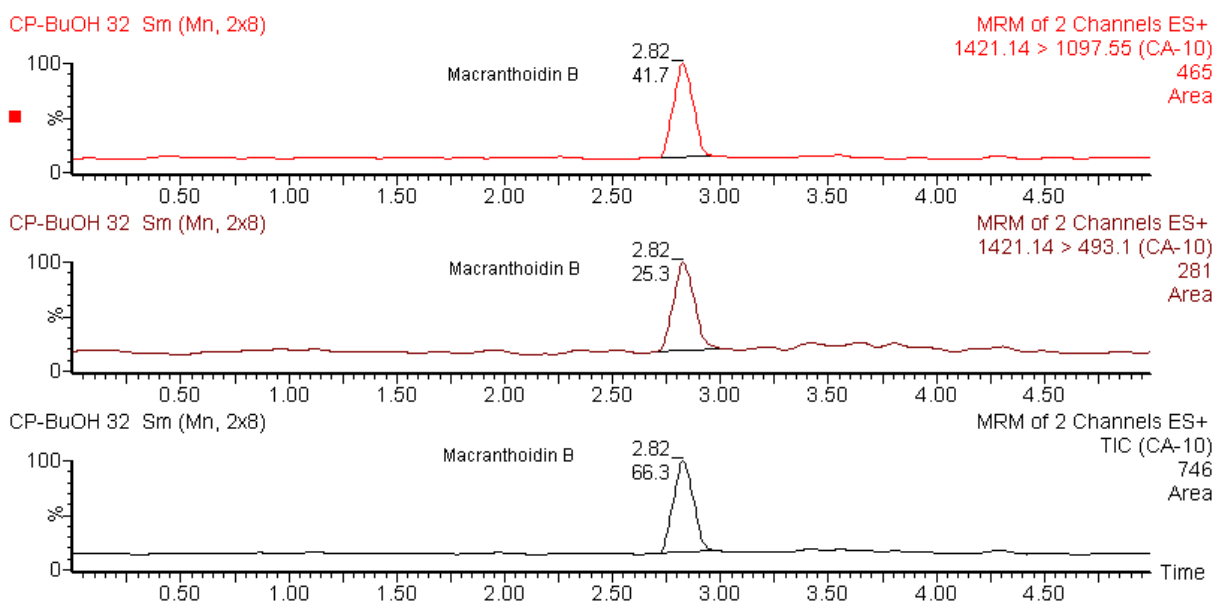


**S 46.** Chromatograms of Sapindoside C ( $m/z$ : 1068.40  $\rightarrow$  1024.26, 1068.40  $\rightarrow$  595.66 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.

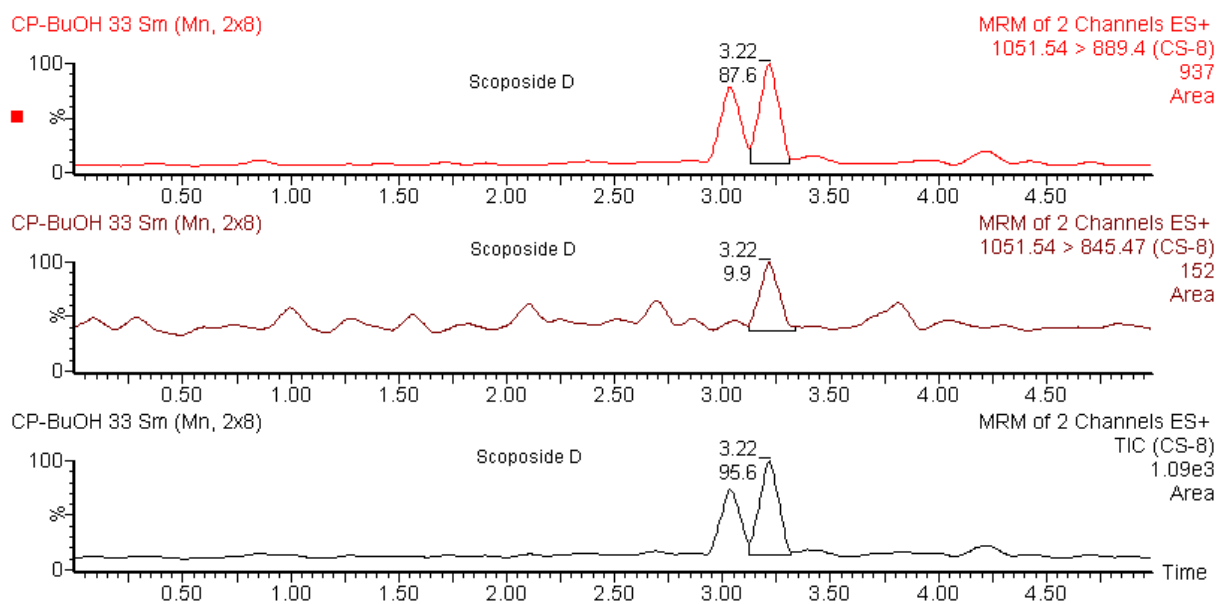




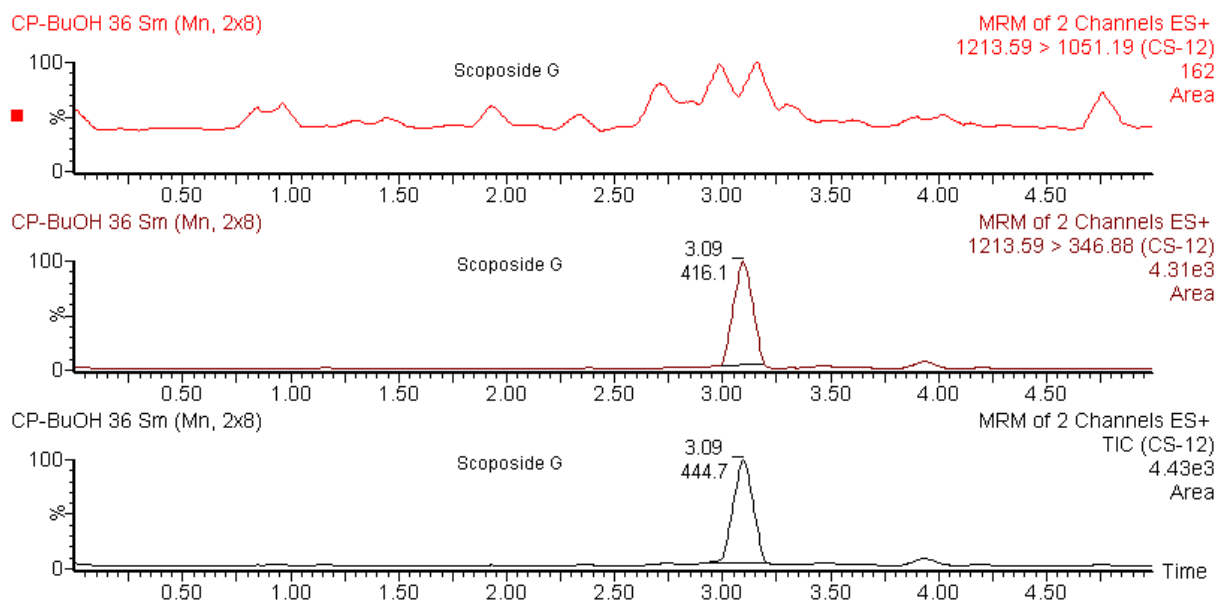
**S 47.** Chromatograms of  $\beta$ -Sitosterol-Glucoside ( $m/z$ : 1175.78  $\rightarrow$  599.03, 1175.78  $\rightarrow$  202.92 and TIC), compound obtained by UPLC-ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



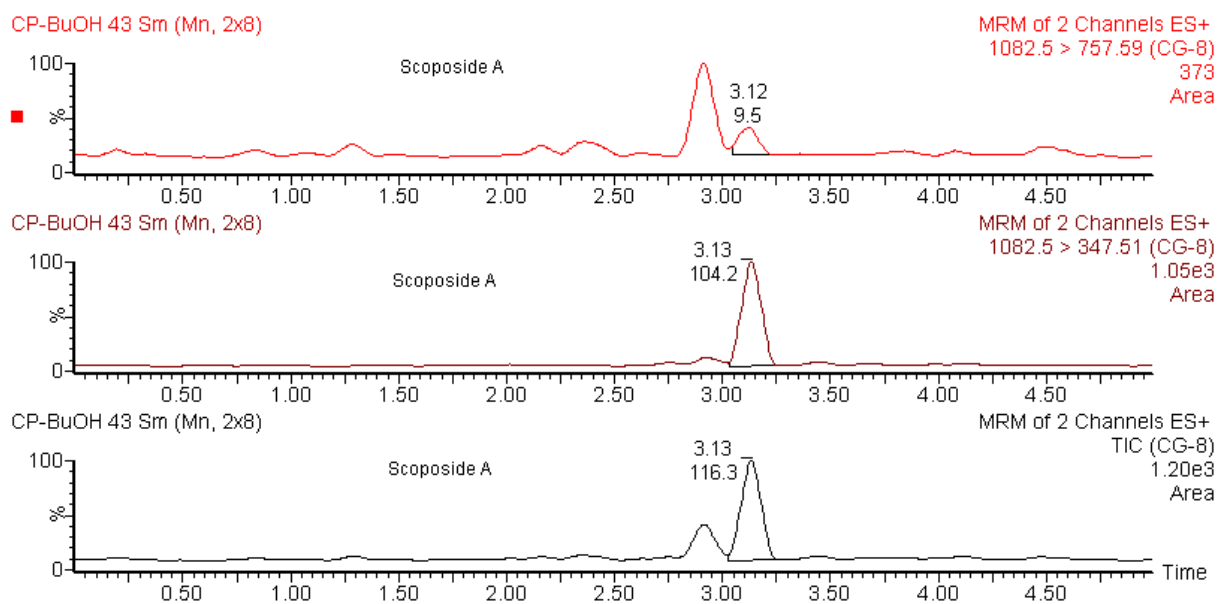
**S 48.** Chromatograms of Macranthoidin B ( $m/z$ : 1421.14  $\rightarrow$  1097.55, 1421.14  $\rightarrow$  493.1 and TIC), compound obtained by UPLC-ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



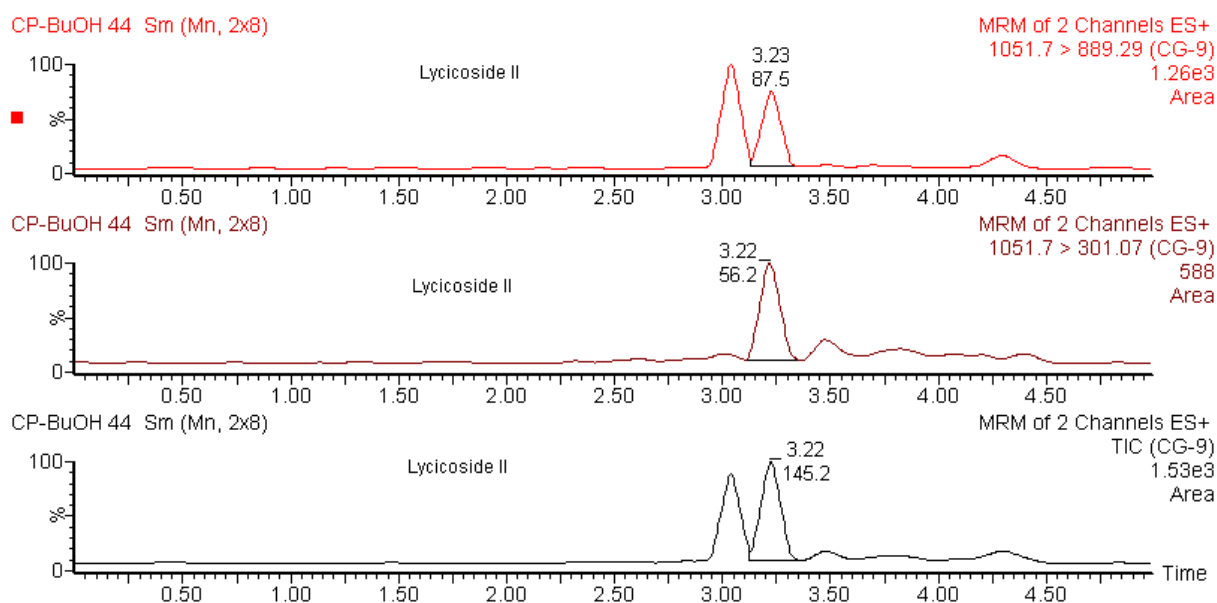
**S 49.** Chromatograms of Scoposide D ( $m/z$ : 1051.54  $\rightarrow$  889.40, 1051.54  $\rightarrow$  845.47 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



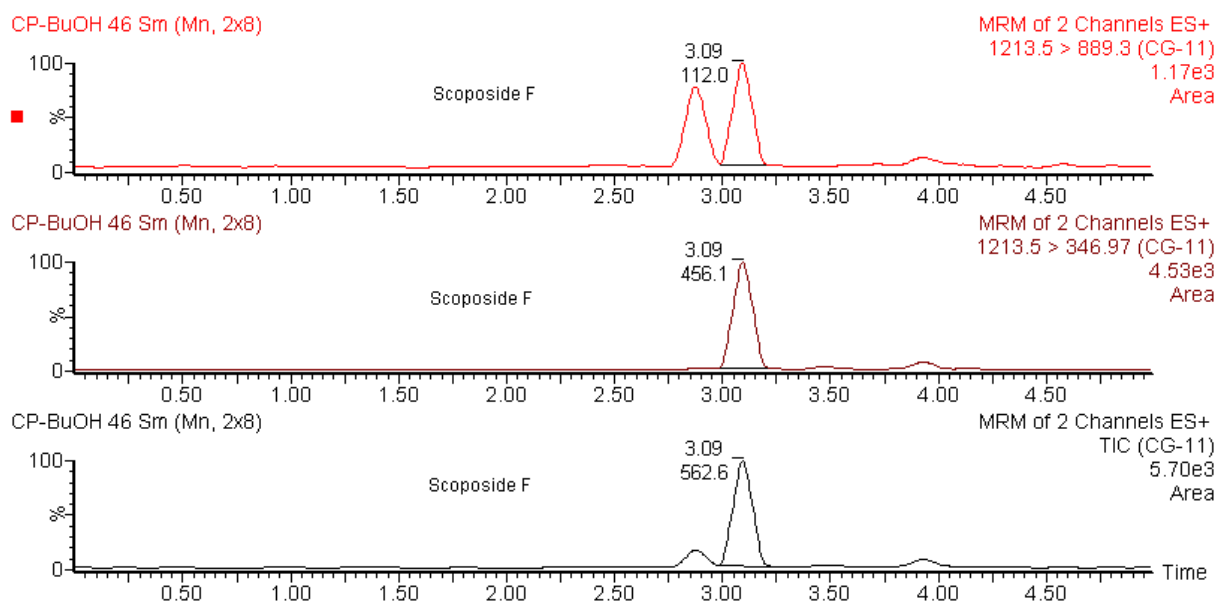
**S 50.** Chromatograms of Scoposide G ( $m/z$ : 1213.59  $\rightarrow$  1051.19, 1213.59  $\rightarrow$  346.88 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



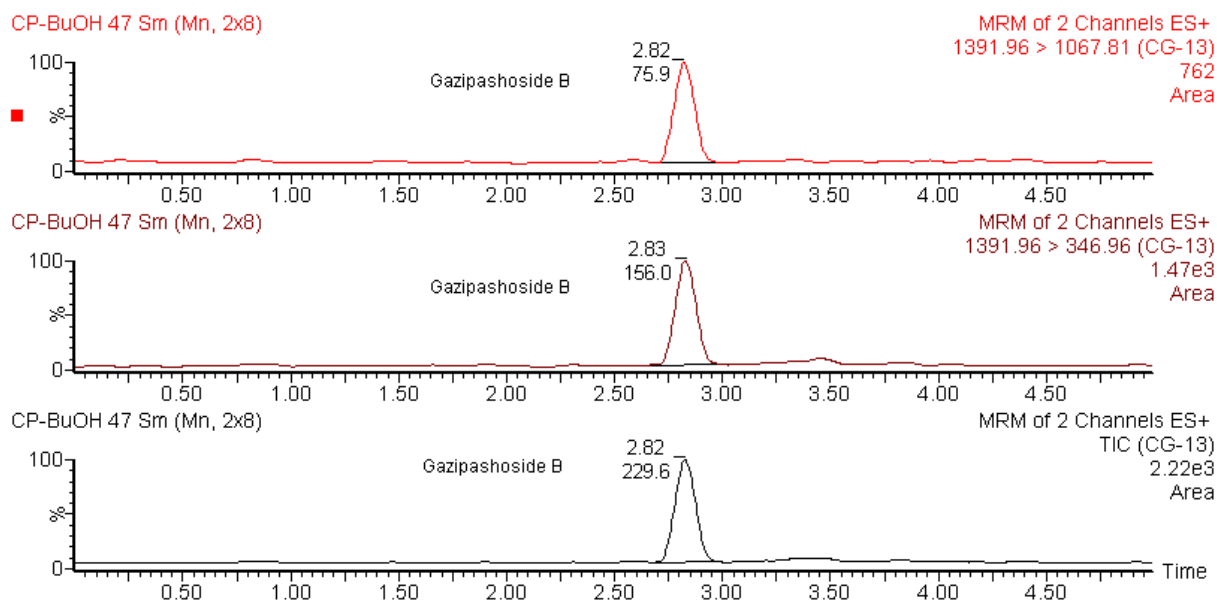
**S 51.** Chromatograms of Scoposide A ( $m/z$ : 1082.50  $\rightarrow$  757.59, 1082.50  $\rightarrow$  347.51 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



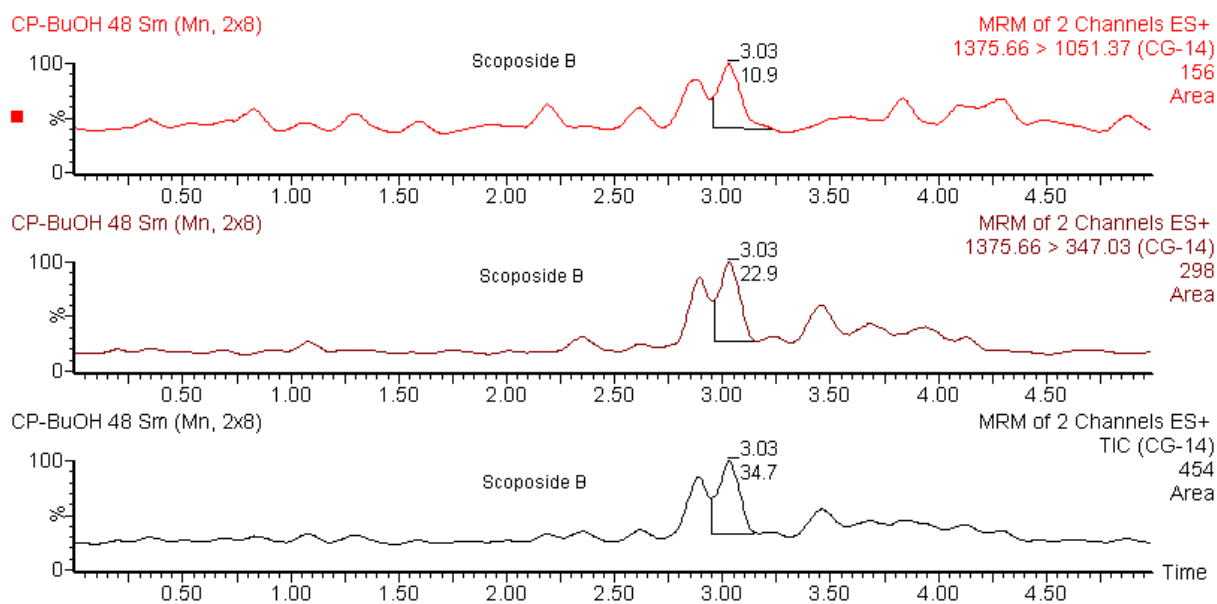
**S 52.** Chromatograms of Lycicoside II ( $m/z$ : 1051.70  $\rightarrow$  889.29, 1051.70  $\rightarrow$  301.07 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



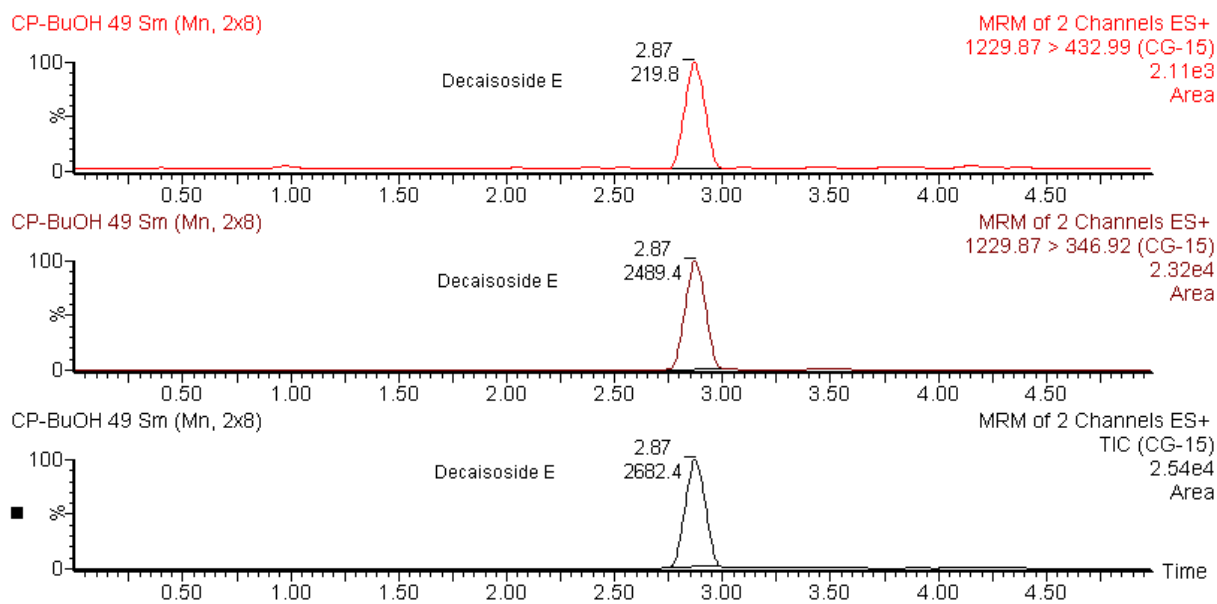
**S 53.** Chromatograms of Scoposide F ( $m/z$ : 1213.50  $\rightarrow$  889.30, 1213.50  $\rightarrow$  346.97 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



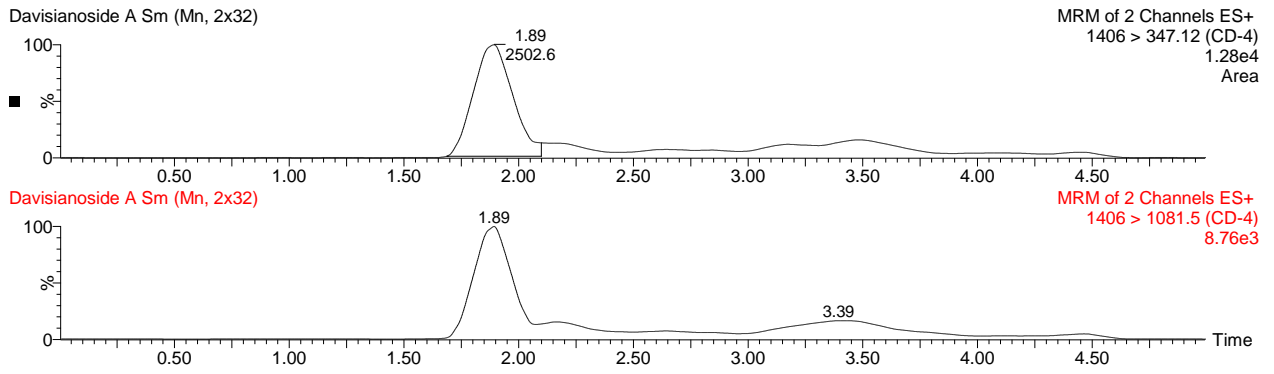
**S 54.** Chromatograms of Gazipashoside B ( $m/z$ : 1391.96  $\rightarrow$  1067.81, 1391.96  $\rightarrow$  346.96 and TIC), compound obtained by UPLC–ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



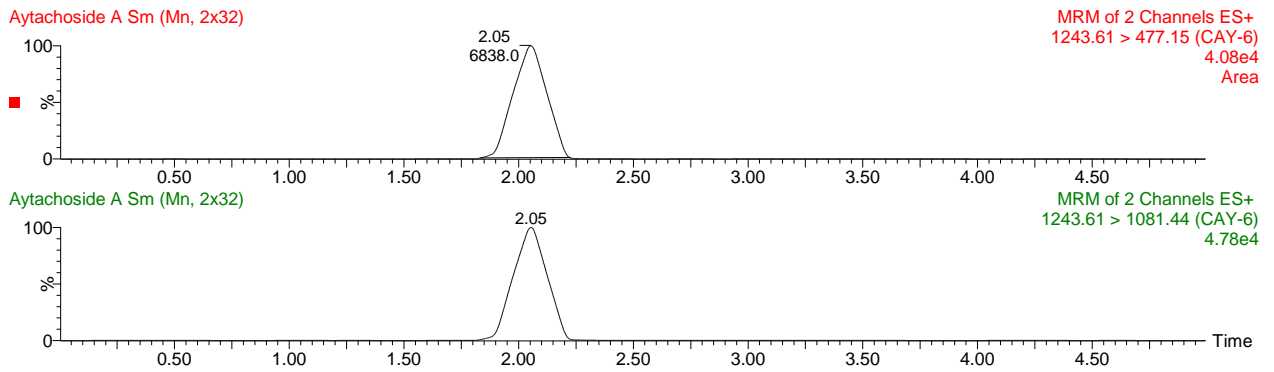
**S 55.** Chromatograms of Scoposide B ( $m/z$ : 1375.66  $\rightarrow$  1051.37, 1375.66  $\rightarrow$  347.03 and TIC), compound obtained by UPLC-ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



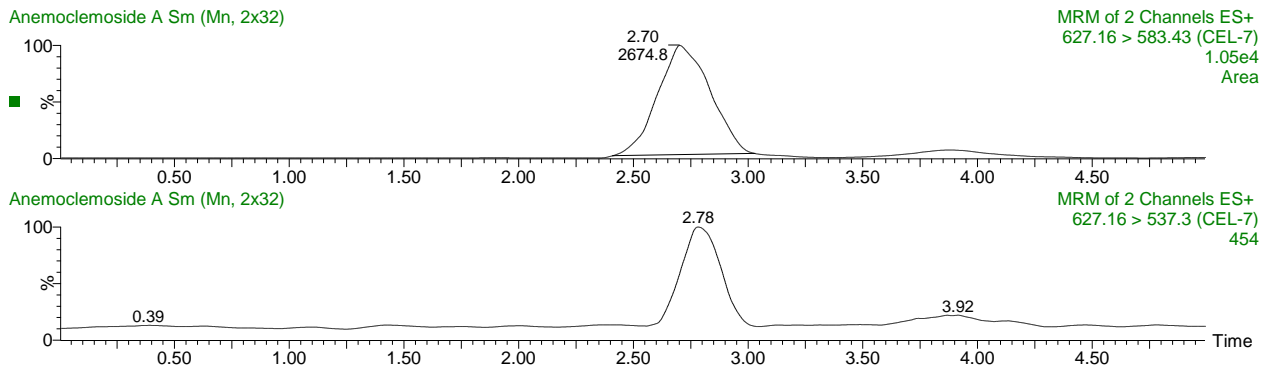
**S 56.** Chromatograms of Decaisoside E ( $m/z$ : 1229.87  $\rightarrow$  432.99, 1229.87  $\rightarrow$  346.92 and TIC), compound obtained by UPLC-ESI-MS-MS in the positive ion mode for crude extract solution in *C. procera*.



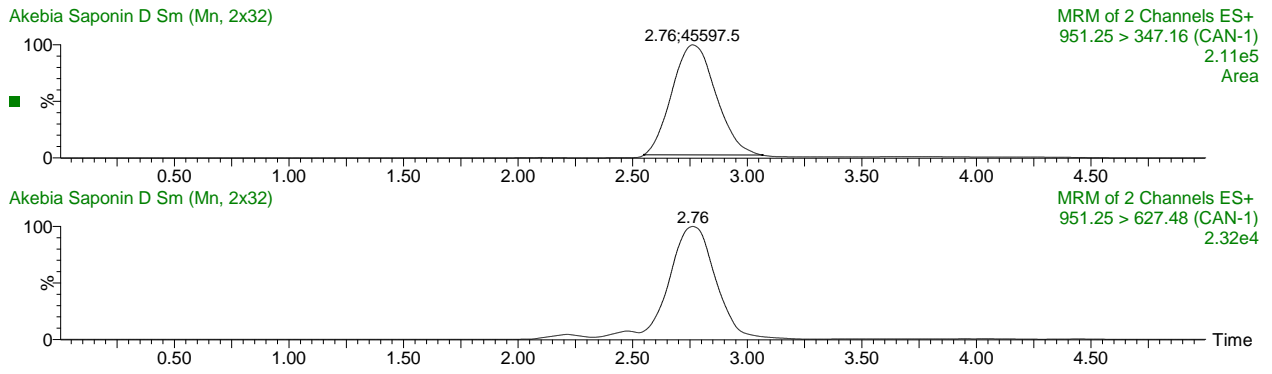
**S 57:** Chromatograms of Davisianoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



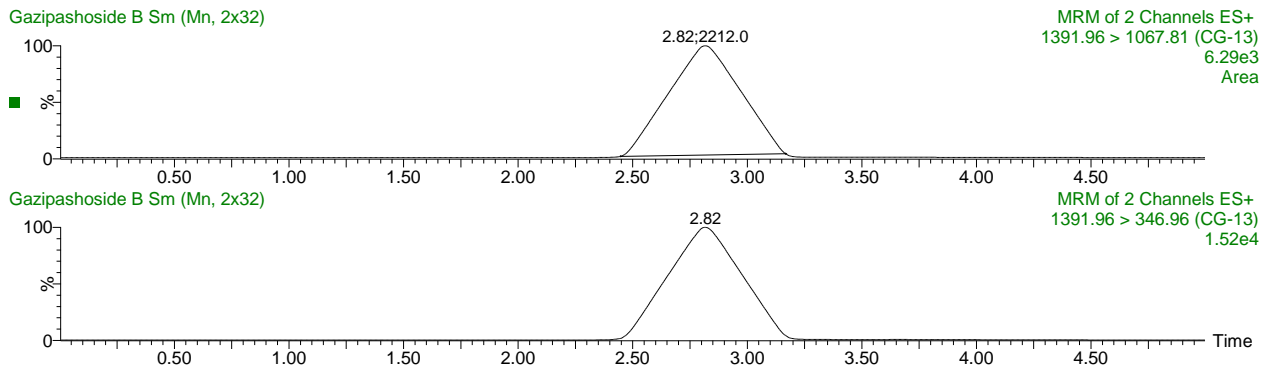
**S 58:** Chromatograms of Aytachoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



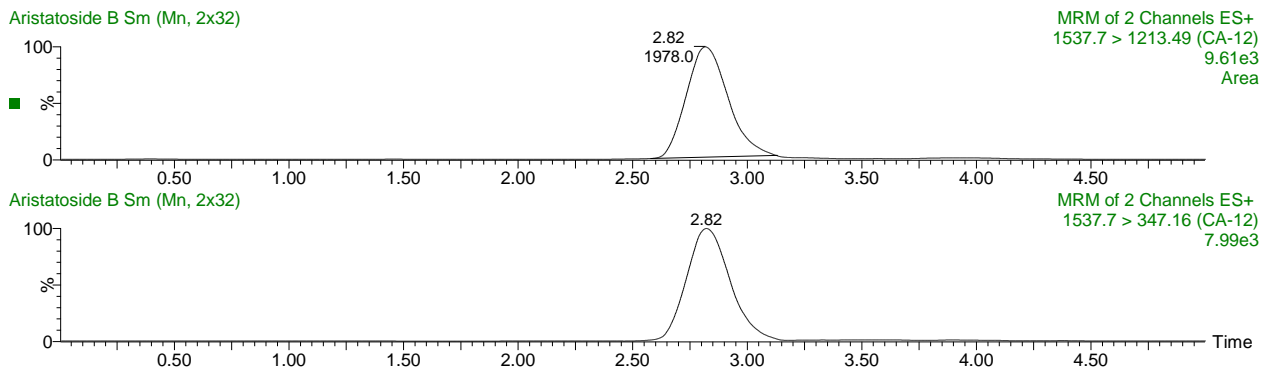
**S 59:** Chromatograms of Anemoclemoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



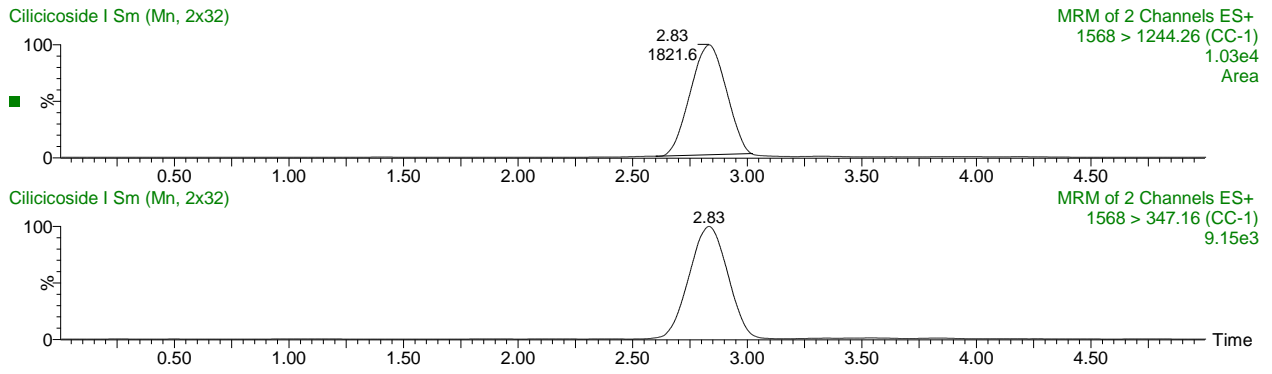
**S 60:** Chromatograms of Akebia Saponin D compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



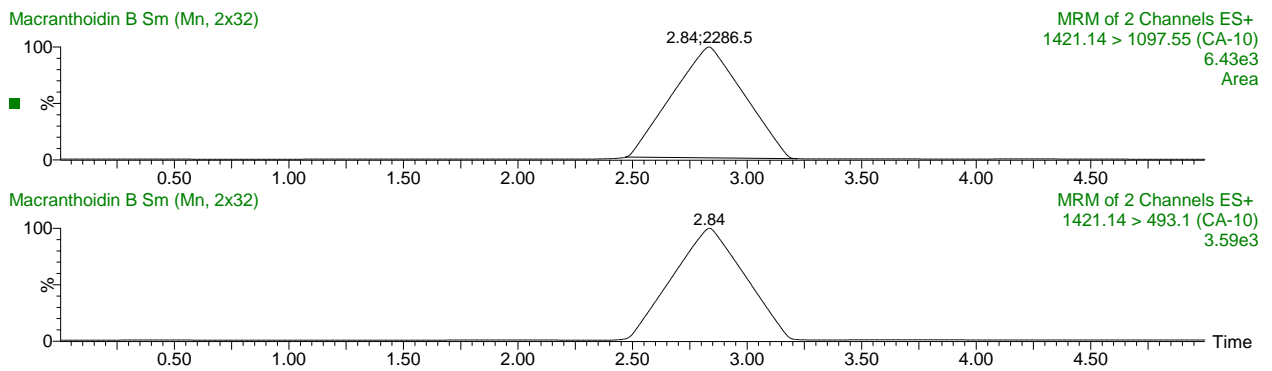
**S 61:** Chromatograms of Gazipashoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



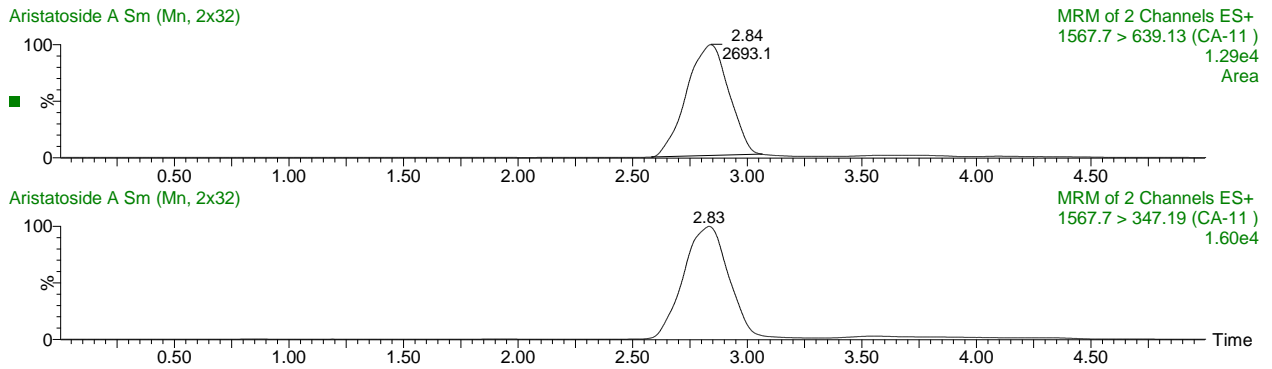
**S 62:** Chromatograms of Aristatoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



**S 63:** Chromatograms of Cilicicoside I compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).

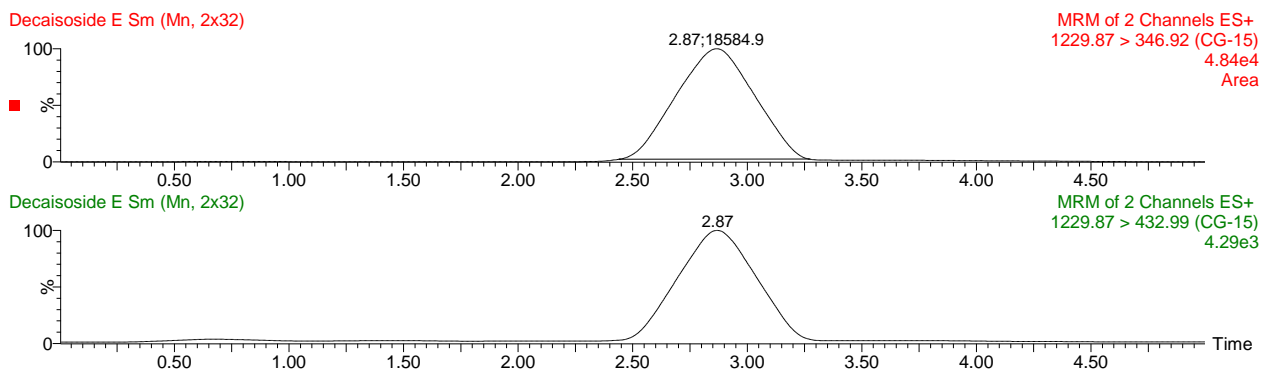


**S 64:** Chromatograms of Macranthoidin B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).

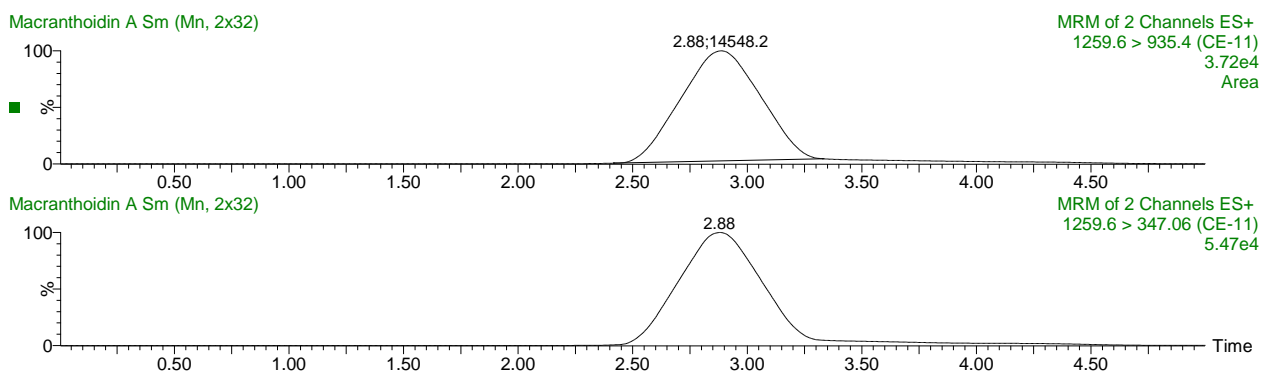


**S 65:** Chromatograms of Aristatoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).

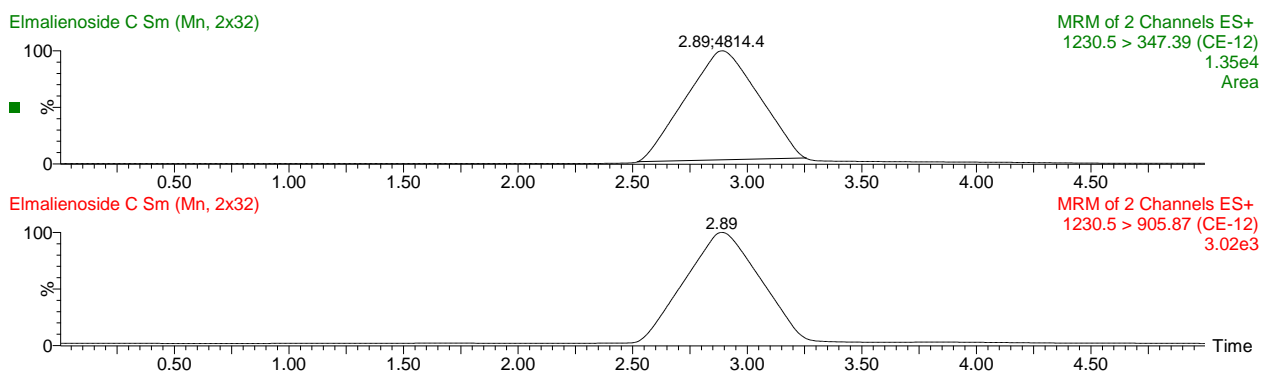




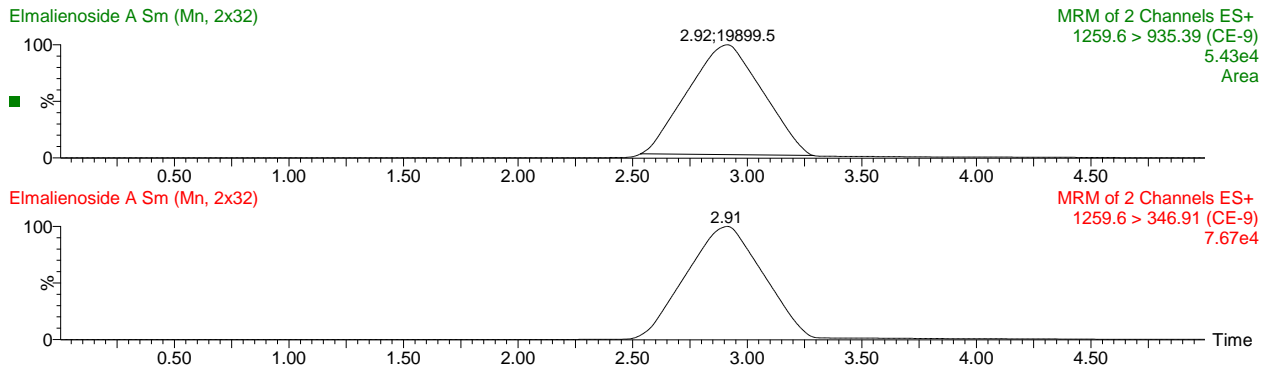
**S 66:** Chromatograms of Decaisoside E compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



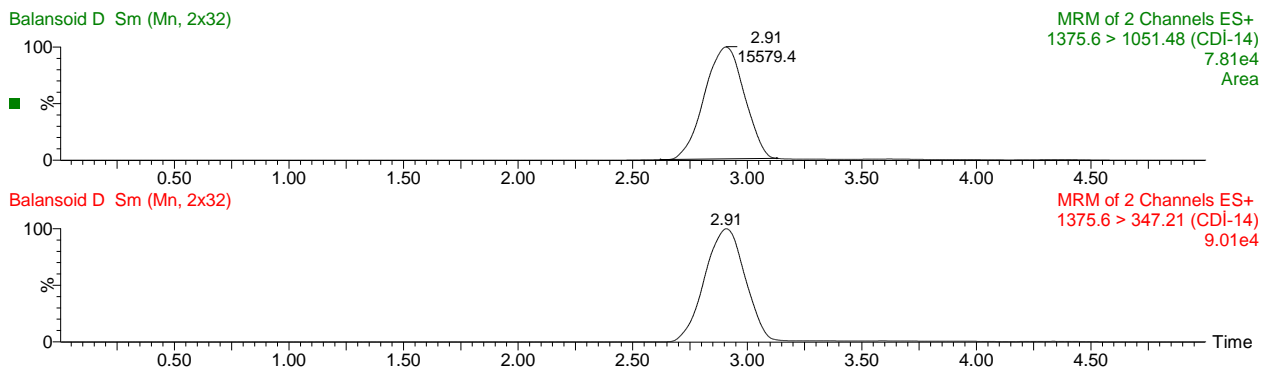
**S 67:** Chromatograms of Macranthoidin A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



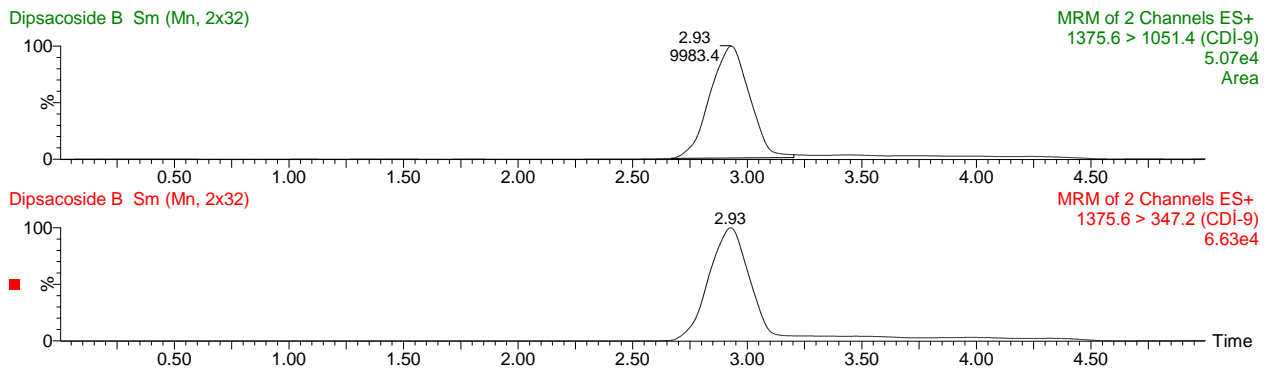
**S 68:** Chromatograms of Elmalienoside C compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



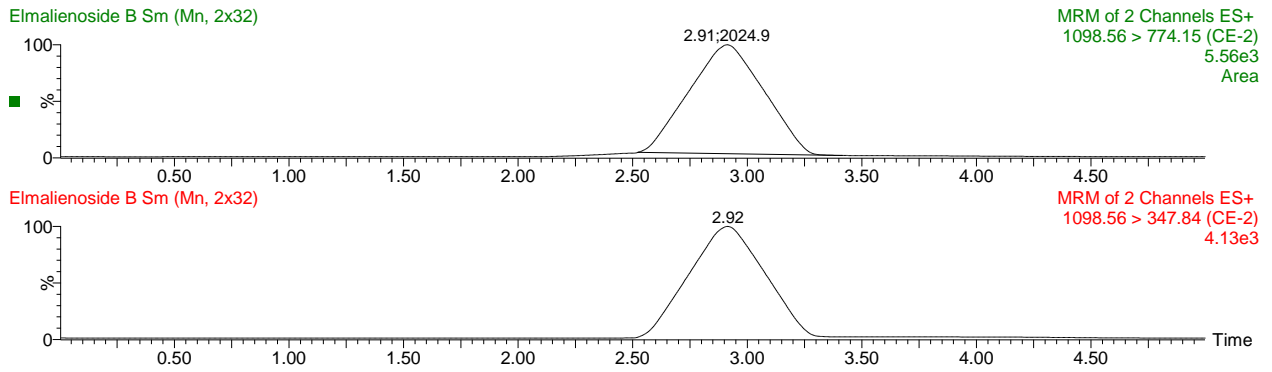
**S 69:** Chromatograms of Elmalienoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



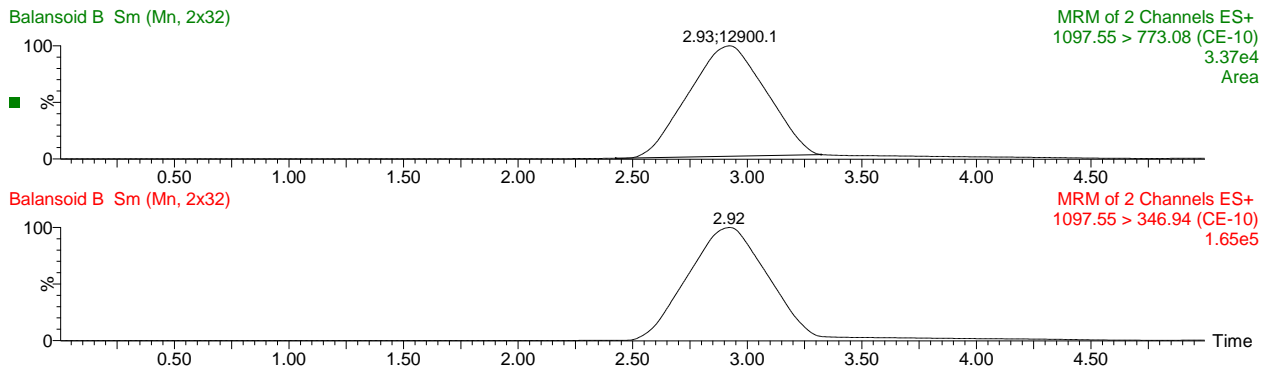
**S 70:** Chromatograms of Balansoid D compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



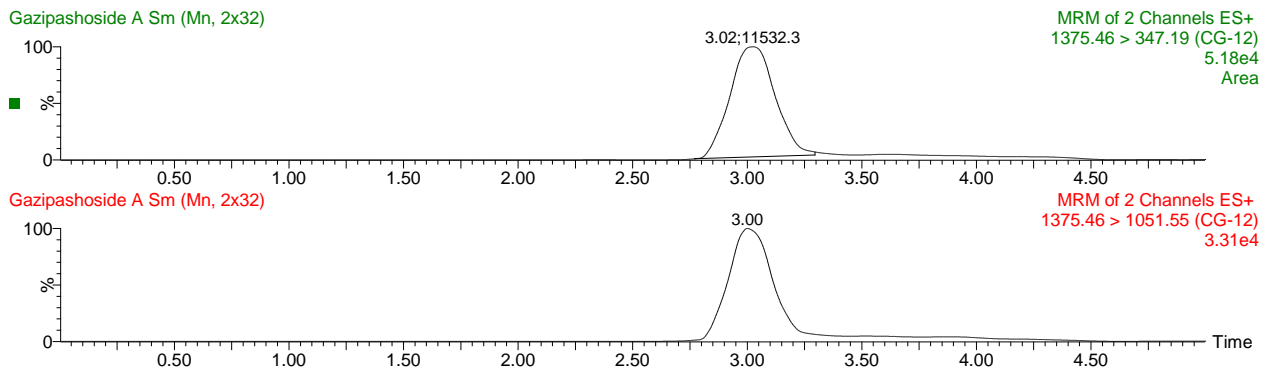
**S 71:** Chromatograms of Dipsacoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



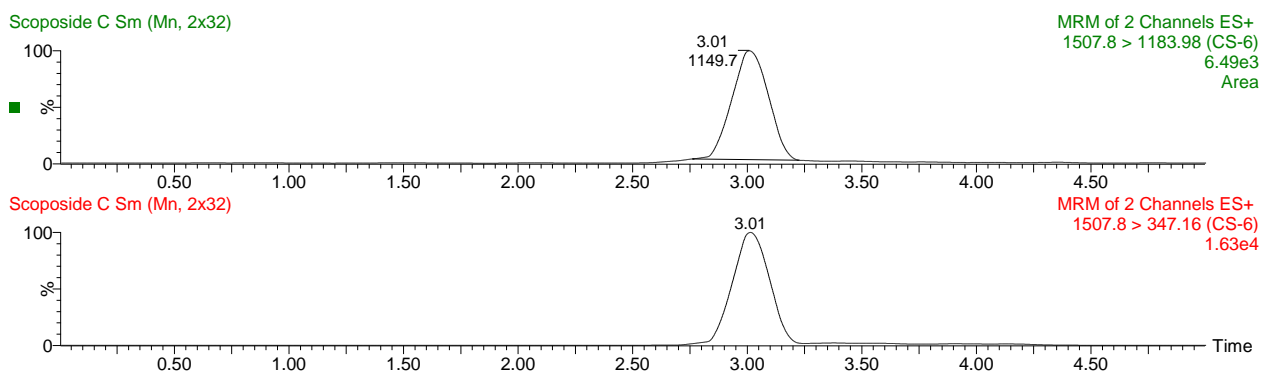
**S 72:** Chromatograms of Elmalienoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



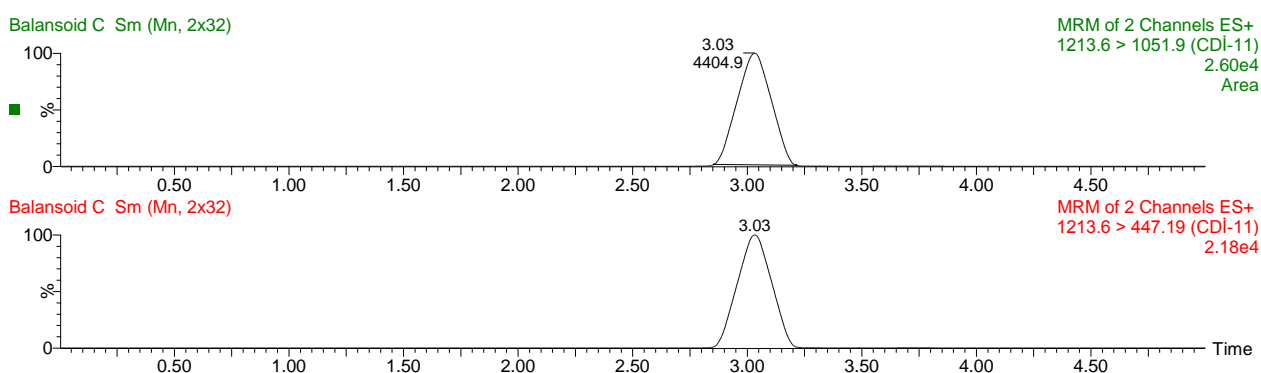
**S 73:** Chromatograms of Balansoid B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



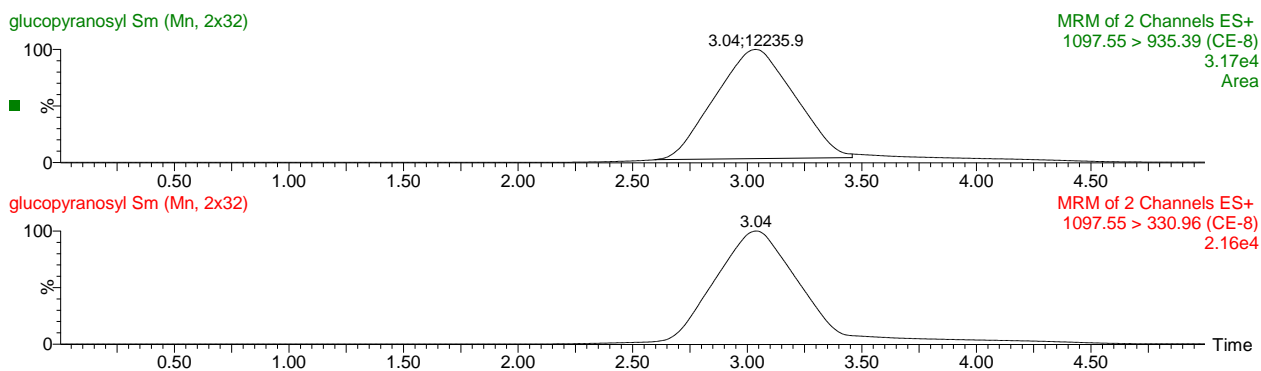
**S 74:** Chromatograms of Gazipashoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



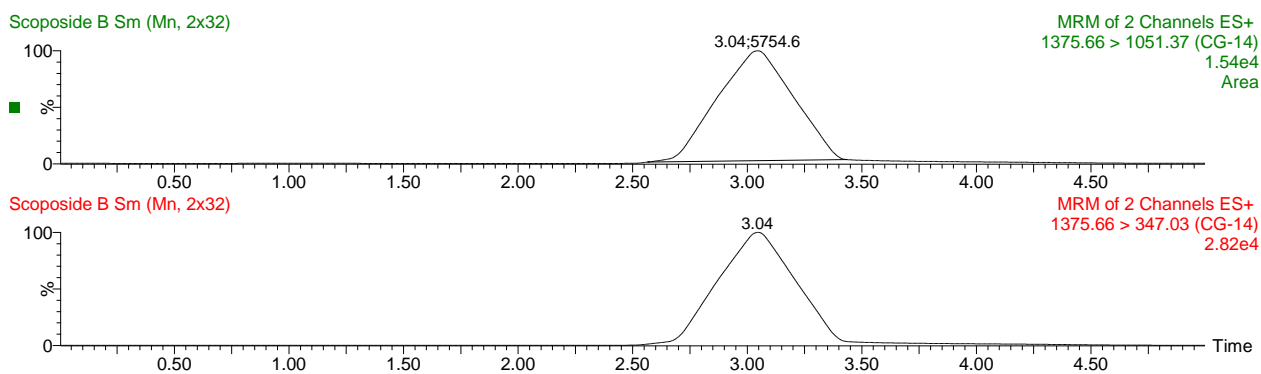
**S 75:** Chromatograms of Scoposide C compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



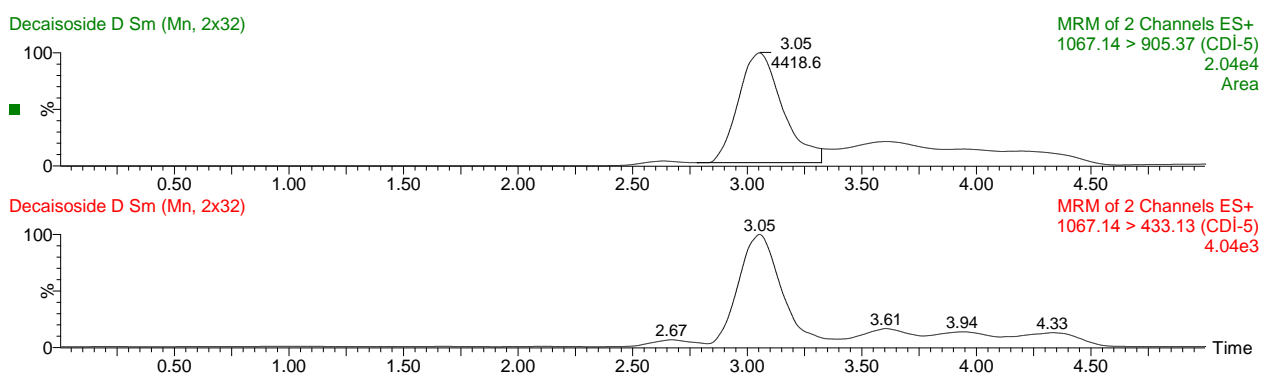
**S 76:** Chromatograms of Balansoid C compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



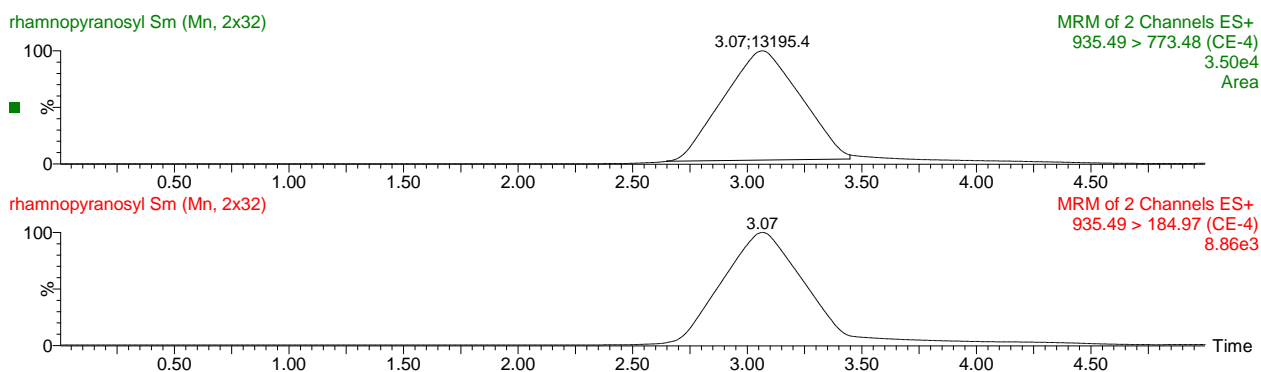
**S 77:** Chromatograms of - 3-O-β-D-glucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L arabinopyranosyl hederagenin 28-O-β-D- glucopyranosyl ester compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



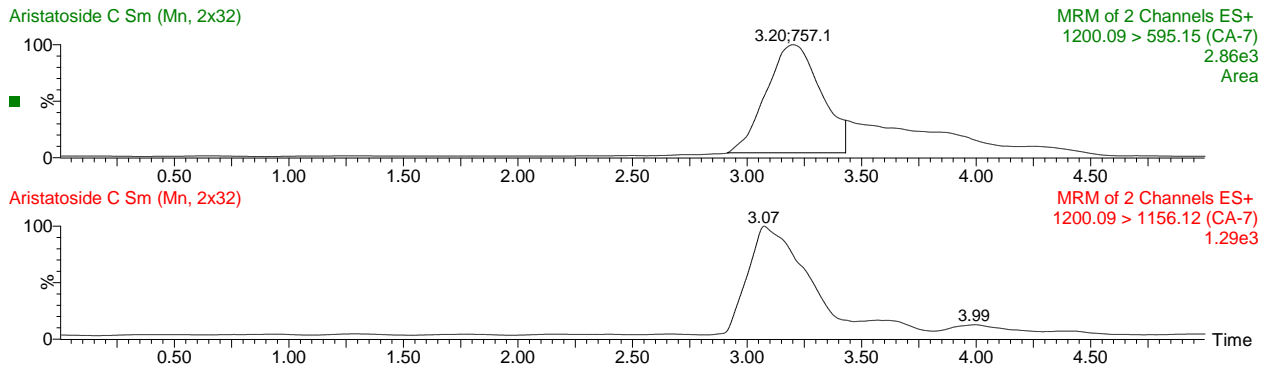
**S 78:** Chromatograms of Scoposide B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



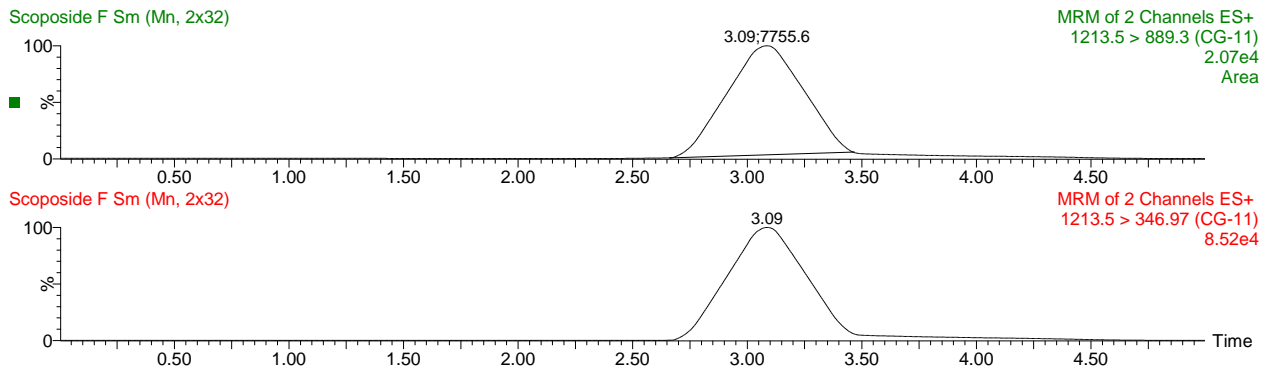
**S 79:** Chromatograms of Decaisoside D compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



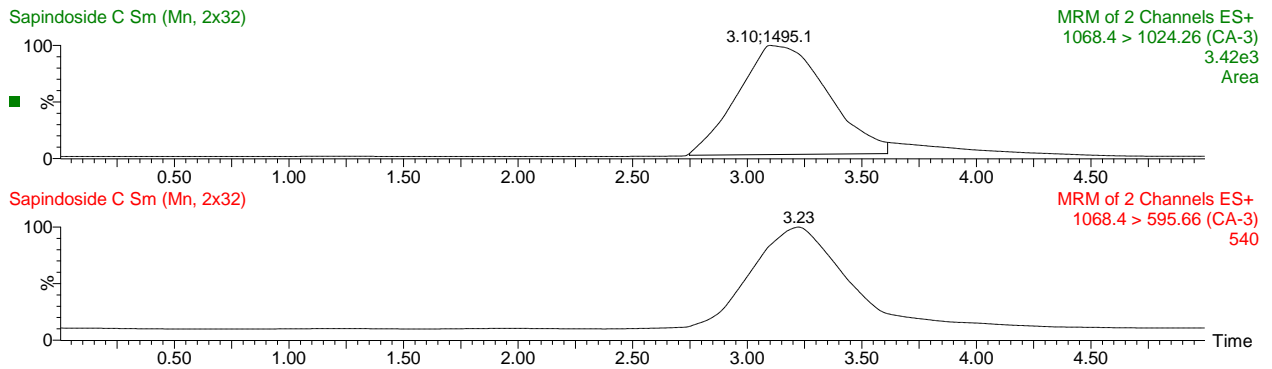
**S 80:** Chromatograms of 3-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- $\alpha$ -L-arabinopyranosyl hederagenin 28-O- $\beta$ -D-glucopyranosyl ester compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



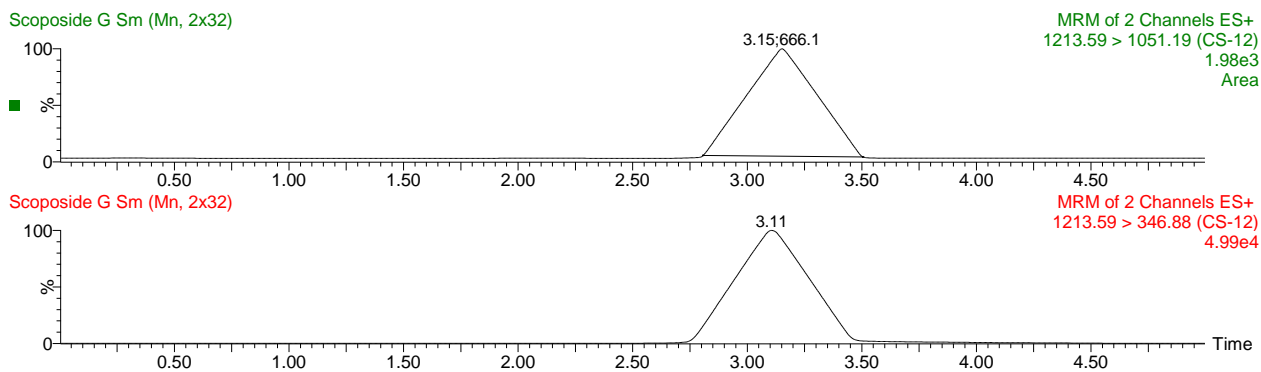
**S 81:** Chromatograms of Aristatoside C compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



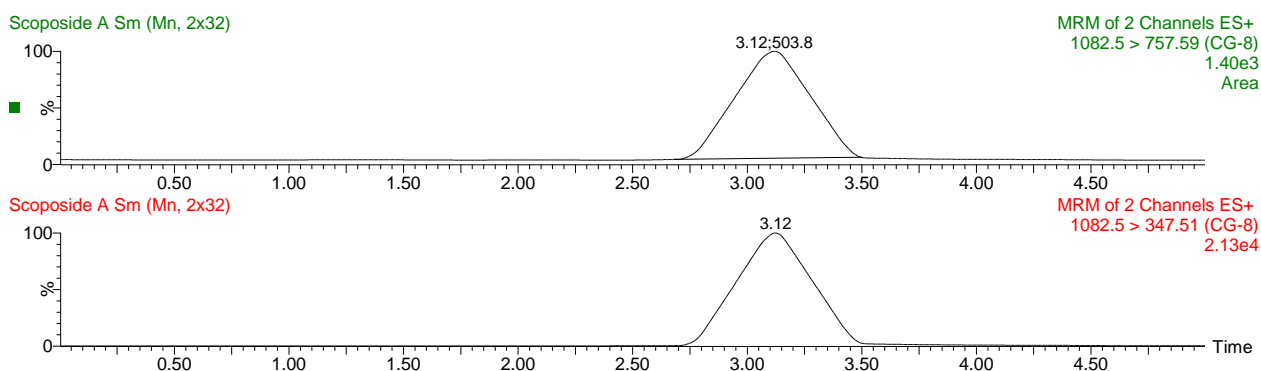
**S 82:** Chromatograms of Scoposide F compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



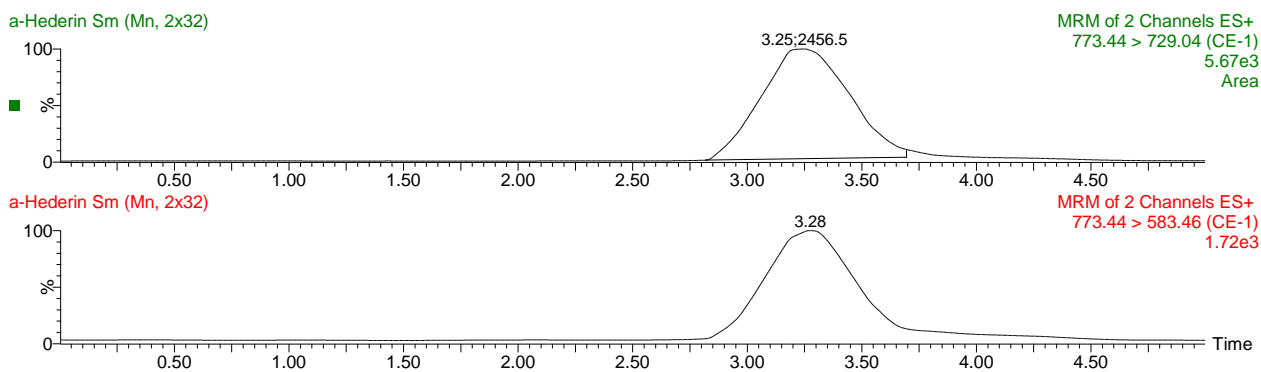
**S 83:** Chromatograms of Sapindoside C compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



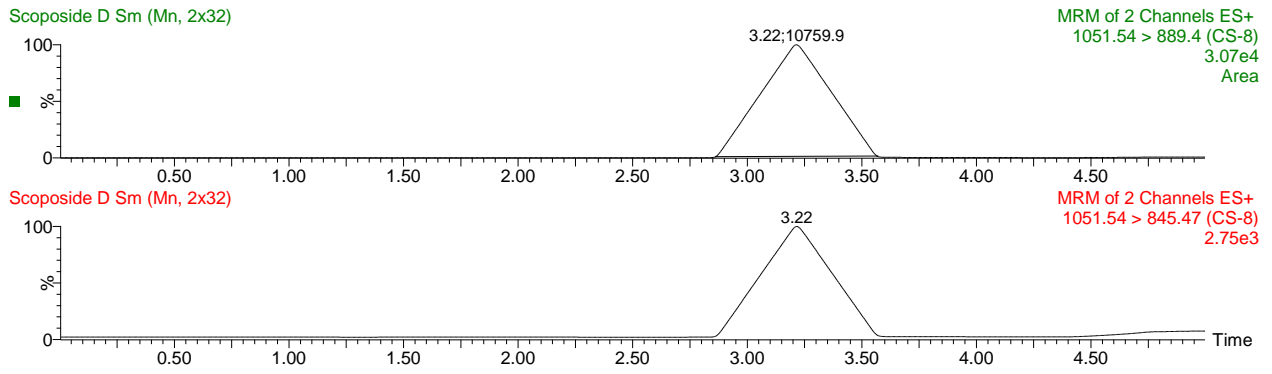
**S 84:** Chromatograms of Scoposide G compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



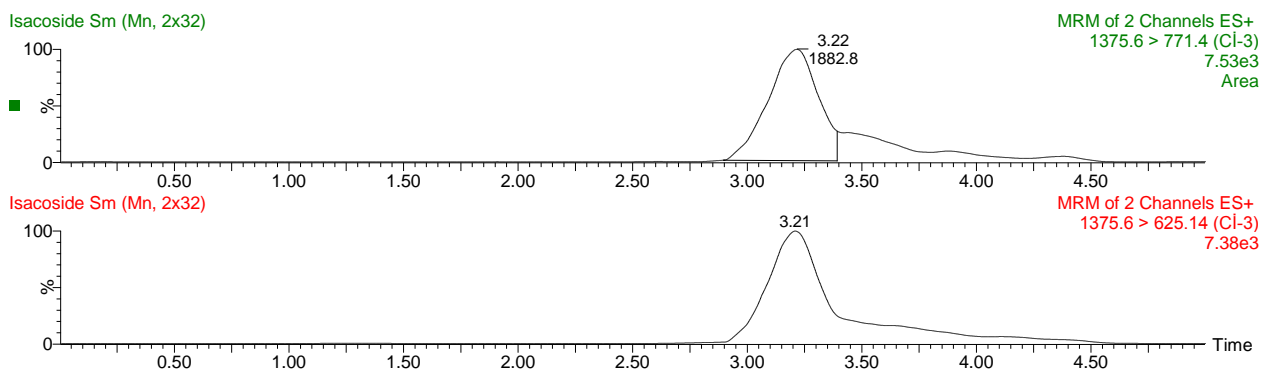
**S 85:** Chromatograms of Scoposide A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



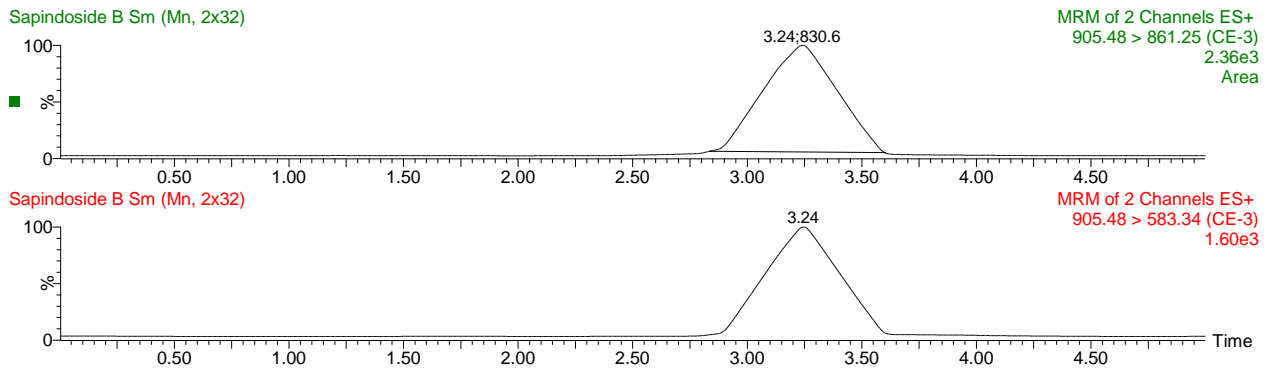
**S 86:** Chromatograms of  $\alpha$ -Hederin compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



**S 87:** Chromatograms of Scoposide D compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).

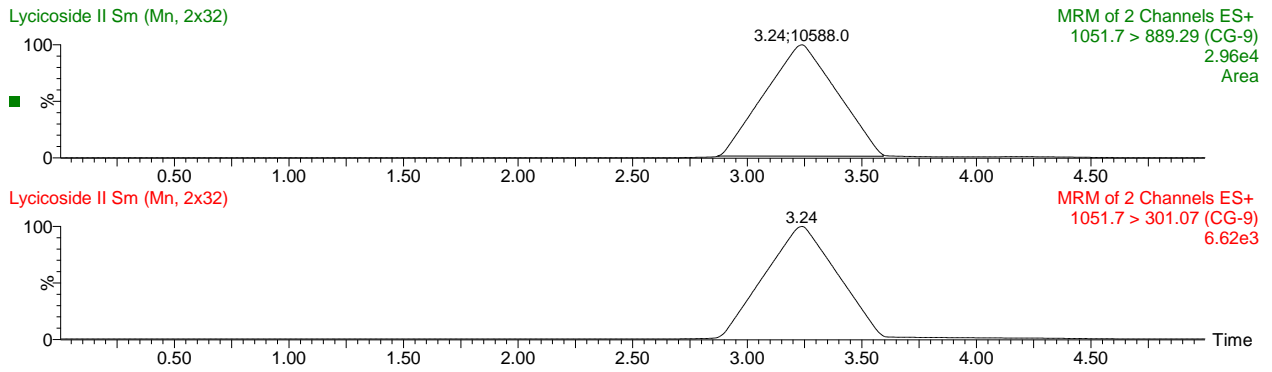


**S 88:** Chromatograms of Isacoside compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).

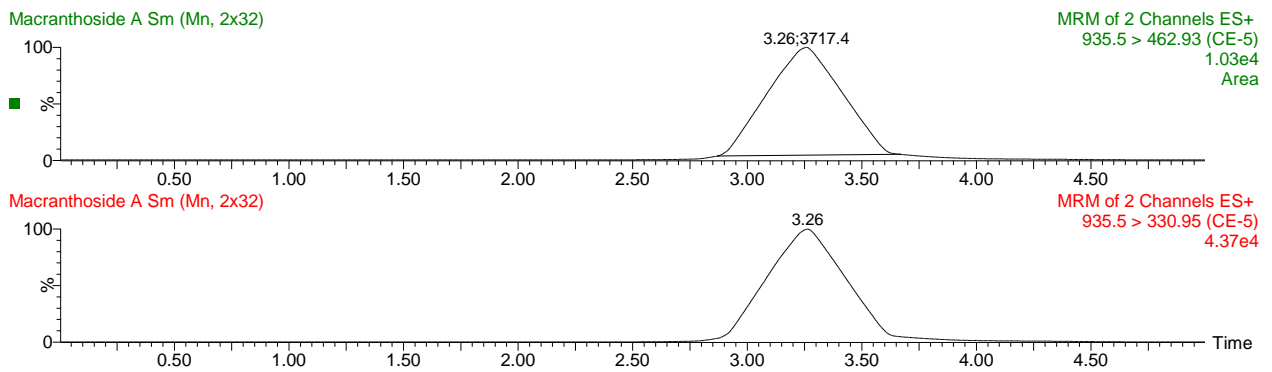


**S 89:** Chromatograms of Sapindoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).

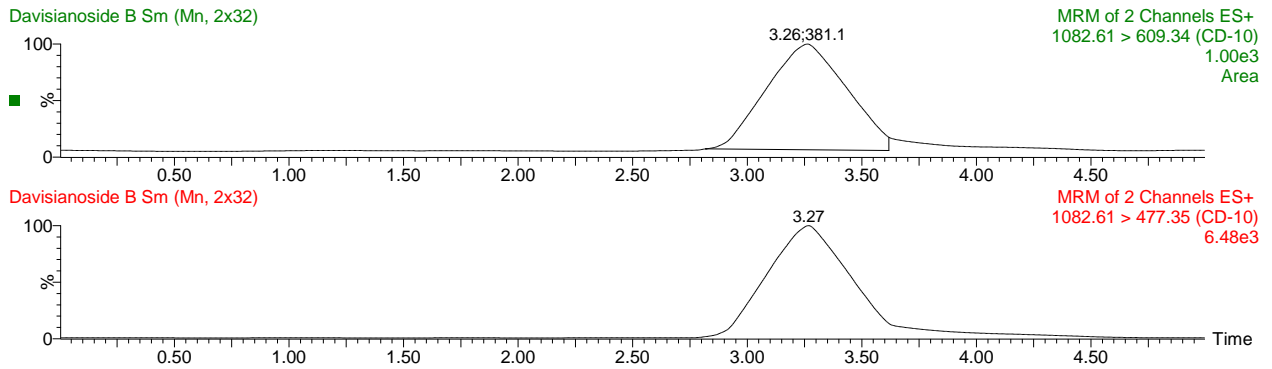




**S 90:** Chromatograms of Lycicoside II compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).

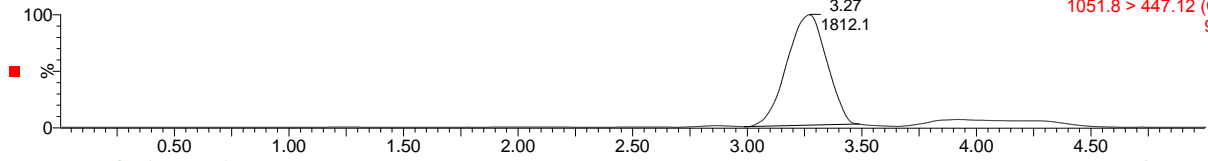


**S 91:** Chromatograms of Macranthoside A compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



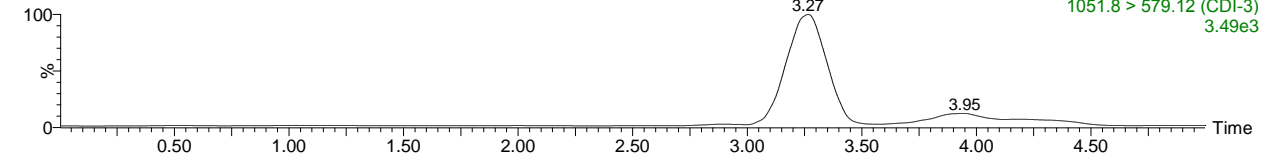
**S 92:** Chromatograms of Davisianoside B compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).

Balansoid A Sm (Mn, 2x32)



MRM of 2 Channels ES+  
1051.8 > 447.12 (CDI-3)  
9.21e3  
Area

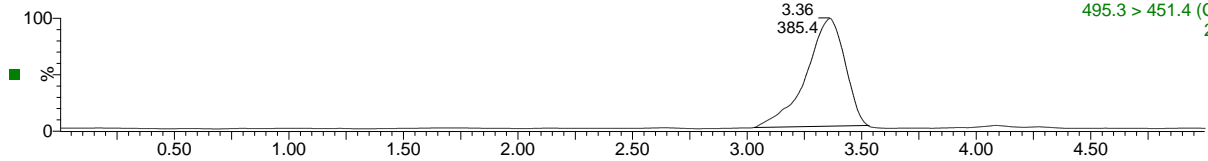
Balansoid A Sm (Mn, 2x32)



MRM of 2 Channels ES+  
1051.8 > 579.12 (CDI-3)  
3.49e3

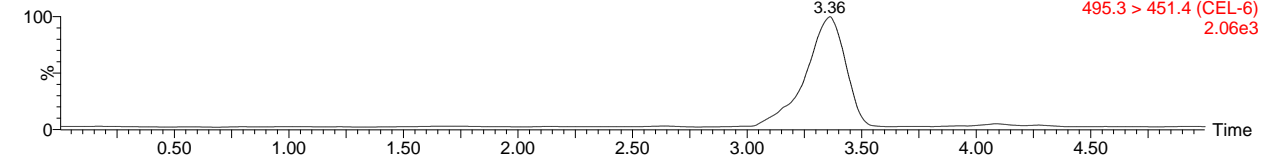
**S 93:** Chromatograms of Balansoid A compound obtained by UPLC-ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).

Hederagenin Sm (Mn, 2x32)



MRM of 1 Channel ES+  
495.3 > 451.4 (CEL-6)  
2.06e3  
Area

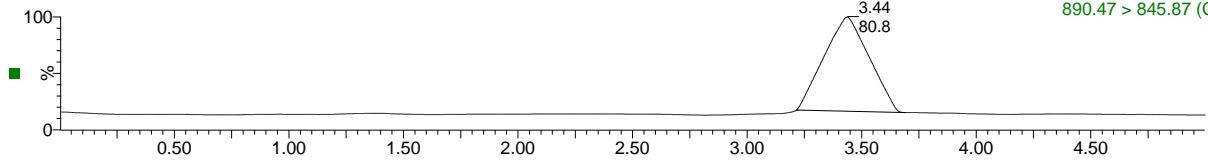
Hederagenin Sm (Mn, 2x32)



MRM of 1 Channel ES+  
495.3 > 451.4 (CEL-6)  
2.06e3

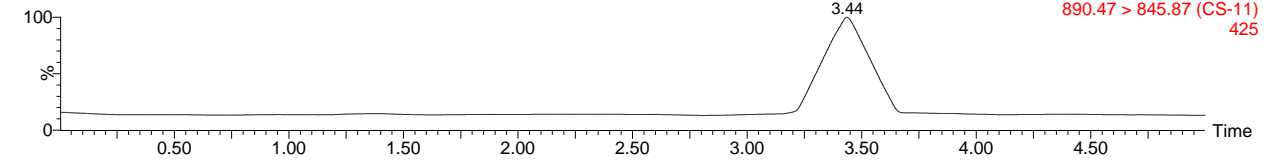
**S 94:** Chromatograms of Hederagenin compound obtained by UPLC-ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).

Scoposide E Sm (Mn, 2x32)



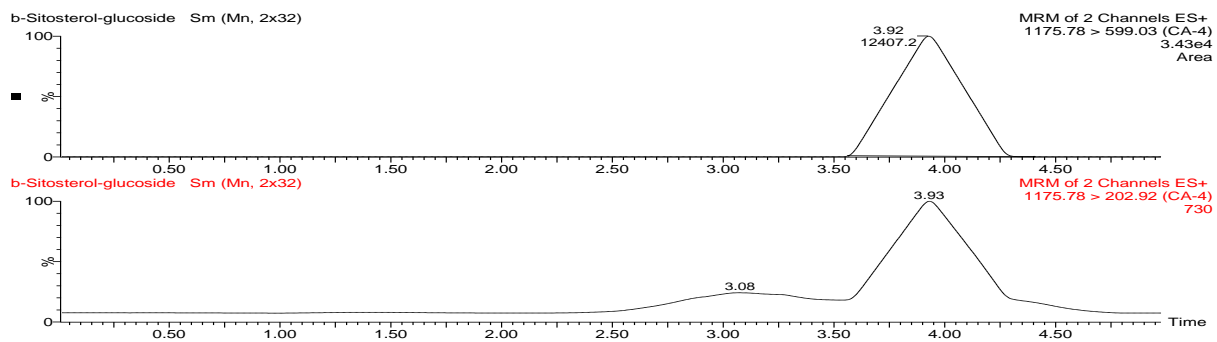
MRM of 1 Channel ES+  
890.47 > 845.87 (CS-11)  
425  
Area

Scoposide E Sm (Mn, 2x32)



MRM of 1 Channel ES+  
890.47 > 845.87 (CS-11)  
425

**S 95:** Chromatograms of Scoposide E compound obtained by UPLC-ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).



**S 96:** Chromatograms of  $\beta$ -Sitosterol glucoside compound obtained by UPLC–ESI-MS-MS in the positive ion mode for standard solution (0.100 mg/L).