

Appendix A

Table A1. Correspondence between numbers, trivial and semisystematic names according to Blažević *et al.* [24] and recommended value UV response factors relative to sinigrin at 229 nm referenced by Clarke [12].

No	Trivial name	Semisystematic name	UV response factors
5	-	4-(Benzoyloxy)butyl GSL	0.3
[10]	Glucomalcolmiin	3-(Benzoyloxy)propyl GSL	0.4
11	Glucotropaeolin	Benzyl GSL	0.95
12	Gluconapin	But-3-enyl GSL	1.11
23	Sinalbin	4-Hydroxybenzyl GSL	0.50
24R	Progoitrin	(2R)-2-Hydroxybut-3-enyl GSL	1.09
24S	Epiprogoitrin	(2S)-2-Hydroxybut-3-enyl GSL	1.09
[26]	-	4-Hydroxybutyl GSL	1.4
28	4-Hydroxyglucobrassicin	4-Hydroxyindol-3-ylmethyl GSL	0.28
38S	Gluconapoleiferin	(2S)-2-Hydroxypent-4-enyl GSL	1.00
40R	Epigluco barbarin	(2R)-2-Hydroxy-2-phenylethyl GSL	1.09
40S	Glucobarbarin	(2S)-2-Hydroxy-2-phenylethyl GSL	1.09
[42]	-	3-Hydroxypropyl GSL	2.1
43	Glucobrassicin	Indol-3-ylmethyl GSL	0.29
46	Glucoaubrietin	4-Methoxybenzyl GSL	-
47	Neoglucobrassicin	1-Methoxyindol-3-ylmethyl GSL	0.20
48	4-Methoxyglucobrassicin	4-Methoxyindol-3-ylmethyl GSL	0.25
56	Glucoputranjivin	1-Methylethyl GSL	1.0
61	Glucocochlearin	(1S)-1-Methylpropyl GSL	-
62	-	2-Methylpropyl GSL	-
64	Glucoraphanin	(R)-4-(Methylsulfinyl)butyl GSL	1.07
65	Glucocamelinin	(R)-10-(Methylsulfinyl)decyl GSL	-
66	-	(R)-7-(Methylsulfinyl)heptyl GSL	1.00
67	Glucohesperin	(R)-6-(Methylsulfinyl)hexyl GSL	1.0
68	Glucoarabin	(R)-9-(Methylsulfinyl)nonyl GSL	1.00
69	Glucohirsutin	(R)-8-(Methylsulfinyl)octyl GSL	1.1
72	Glucoalyssin	(R)-5-(Methylsulfinyl)pentyl GSL	1.07
73	Glucoiberin	(R)-3-(Methylsulfinyl)propyl GSL	1.07
77	-	10-(Methylsulfonyl)decyl GSL	-
79	-	9-(Methylsulfonyl)nonyl GSL	-
80	-	8-(Methylsulfonyl)octyl GSL	-
84	Glucoerucin	4-(Methylsulfonyl)butyl GSL	1.04
87	-	7-(Methylsulfonyl)heptyl GSL	1.0
92	-	8-(Methylsulfonyl)octyl GSL	1.1
94	Glucoberteroin	5-(Methylsulfonyl)pentyl GSL	-
95	Glucoibervirin	3-(Methylsulfonyl)propyl GSL	0.8
101	Glucobrassicinapin	Pent-4-enyl GSL	1.15
105	Gluconasturtiin	2-Phenylethyl GSL	0.95
107	Sinigrin	Prop-2-enyl GSL	1.00
117	-	5-(Benzoyloxy)pentyl GSL	-

Blažević number (No). Glucosinolate (GSL). Glucosinolates partially characterized with reasonable evidence for one single structure to be naturally biosynthesized in plants [in brackets].

Eq. A1. The glucosinolates results were expressed in mmol.kg^{-1} of DM (following the standard) with this formula.

$$\left(\frac{\left(\frac{AUC - b}{a} \right)}{Q} \right) * V$$

AUC = sum of corrected area (total glucosinolates content) or individual corrected area (individual glucosinolate content)

b = interception of desulfo-sinigrin calibration curve (μM)

a = slope of desulfo-sinigrin calibration curve (μM)

Q = starting material in mg of DM

V = final volume for HPLC in mL

Eq. A2. The camalexin results were expressed in $\mu\text{g.g}^{-1}$ of DM with this formula.

$$\left(\frac{\left(\frac{AUC - b}{a} \right)}{Q} \right) * V$$

AUC = area under the curve of camalexin

b = interception of camalexin calibration curve ($\mu\text{g.mL}^{-1}$)

a = slope of camalexin calibration curve ($\mu\text{g.mL}^{-1}$)

Q = starting material in g of DM

V = final volume for HPLC in mL

Fig. A1. Calibration curve of sinigrin.

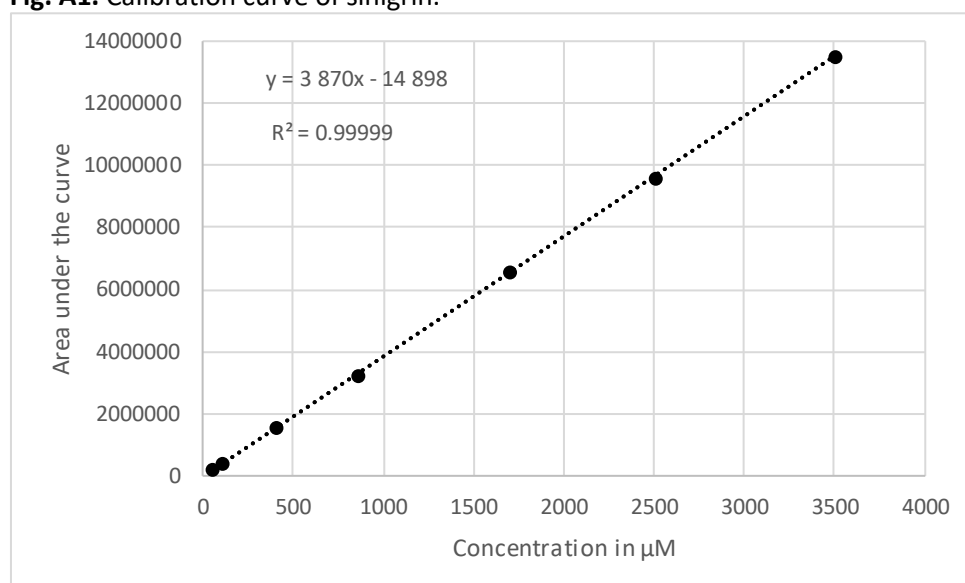
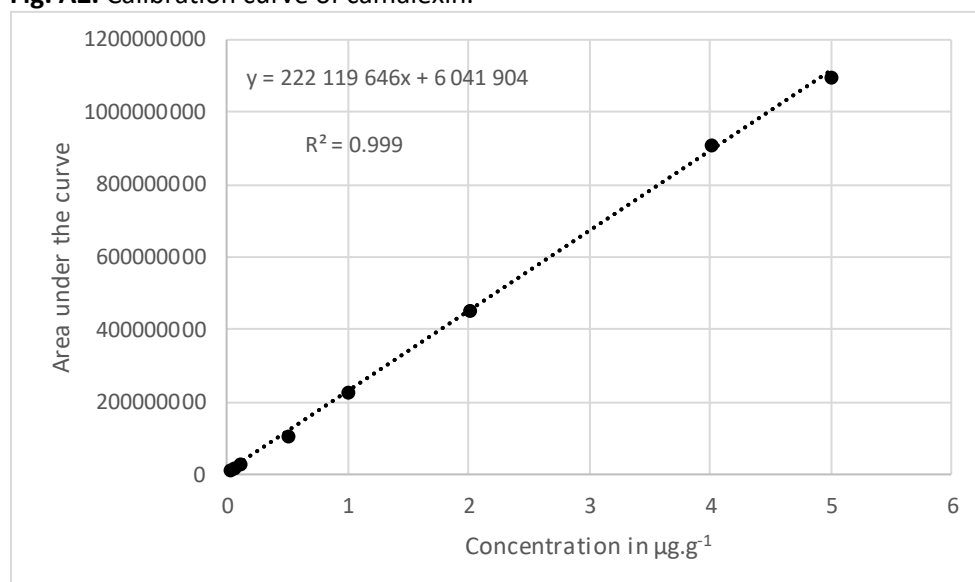


Table A2. Glucosinolates LOD and LOQ calculation.

	Real concentration in μM	Area under the curve	Calculated concentration in μM
1	50	184767	51.6
2	50	188369	52.5
3	50	182870	51.1
4	50	176052	49.3
5	50	187305	52.2
		Mean	51.4
		SD	1.3
		LOD (3 x SD)	3.8
		LOQ (10 x SD)	12.6

Fig. A2. Calibration curve of camalexin.**Table A3.** Camalexin LOD and LOQ calculation.

	Real concentration in $\mu\text{g.mL}^{-1}$	Area under the curve	Calculated concentration in $\mu\text{g.mL}^{-1}$
1	0.025	9845972	0.017
2	0.025	12412718	0.029
3	0.025	12229072	0.028
4	0.025	11763576	0.026
5	0.025	11538550	0.025
		Moyenne	0.025
		SD	0.005
		LOD (3 x SD)	0.014
		LOQ (10 x SD)	0.046

Table A4. Retention times and MS data of (tentatively) identified glucosinolates.

Rt	No	MS ¹ m/z	MS ² m/z
3.6	[42]	[M+H] ⁺ 297.8 [M+Na] ⁺ 319.8 [M-H] ⁻ 295.7 [M+Cl] ⁻ 331.7 [2M-H] ⁻ 592.8	POS: 218.8(100)/184.9(76)/157.9(94)
3.9	73	[M+H] ⁺ 344.4 [M+Na] ⁺ 366.2 [M-H] ⁻ 342.0 [M+Cl] ⁻ 377.2	POS: 242.9(100)/326.6(40)
5.0	[26]	[M+H] ⁺ 311.9 [M+Na] ⁺ 333.8 [M-H] ⁻ 309.7 [M+Cl] ⁻ 345.8 [2M-H] ⁻ 620.6	POS: 218.8(84)/202.8(10)/184.9(89)/171.9(100) NEG: 147.7(100)
5.5	24R	[M+H] ⁺ 309.8 [M+Na] ⁺ 331.8 [M-H] ⁻ 307.7 [2M-H] ⁻ 616.5	POS: 271.8(23)/147.8 (100)/130.0(59)
6.2	64	[M+H] ⁺ 357.8 [M+Na] ⁺ 379.9 [2M+H] ⁺ 737.0 [M-H] ⁻ 355.7 [M+Cl] ⁻ 391.8 [2M-H] ⁻ 712.6	POS: 315.8(13)/217.9(100)/183.9(15) NEG: 193.7(100)/129.9(12)
6.3	24S	[M+H] ⁺ 309.8 [M+Na] ⁺ 331.8 [M-H] ⁻ 307.7 [2M-H] ⁻ 616.7	NEG: 194.6(100)/145.7(40)
6.9	107	[M+H] ⁺ 279.8 [M+Na] ⁺ 301.8	POS: 218.9(100)/202.8(15)/184.8(23) NEG: 274.3(16)/194.6(100)

		[M-H] ⁻ 277.7 [M+Cl] ⁻ 313.6 [2M-H] ⁻ 556.6	
8.5	72	[M+H] ⁺ 371.9 [M+Na] ⁺ 393.8 [M-H] ⁻ 369.7 [M+Cl] ⁻ 405.7	NEG: 207.6(100)/143.8(14)
8.9	38S	[M+H] ⁺ 323.8 [M+Na] ⁺ 345.8 [M-H] ⁻ 321.7 [2M-H] ⁻ 644.6	POS: 275.8(17)/184.8(100)/183.8(55)
9.4	56	[M+H] ⁺ 281.8 [M-H] ⁻ 279.6	
9.6	23	[M+H] ⁺ 345.8 [M+Na] ⁺ 367.8 [M-H] ⁻ 343.7 [M+Cl] ⁻ 379.8	POS: 183.8(100)/149.2(40)/107.2(43) NEG: 181.6(100)
10.9	12	[M+H] ⁺ 293.8 [M+Na] ⁺ 315.8 [M-H] ⁻ 291.7 [2M-H] ⁻ 584.5	POS: 218.7(100)/202.8(32)/184.8(14) NEG: 194.7(100)
11.4	67	[M+H] ⁺ 385.8 [M+Na] ⁺ 407.7 [M-H] ⁻ 383.8 [M+Cl] ⁻ 419.8	POS: 352.9(21)/223.8(100)/174.0(25)/155.9(64) NEG: 221.6(100)/157.8(17)
12.2	28	[M+H] ⁺ 384.8 [M-H] ⁻ 382.7	POS: 222.8(100)/171.8(10) NEG: 220.6(100)/204.6(15)/168.6(24)
12.3	95	[M+H] ⁺ 327.8 [M-H] ⁻ 325.8 [M+Cl] ⁻ 361.7 [2M-H] ⁻ 652.8	POS: 165.9(100)/147.9(18)/118.0(51) NEG: 163.7(100)
12.6	61	[M-H] ⁻ 293.7 [M+Cl] ⁻ 329.8	

13.1	40R	[M+H] ⁺ 359.8 [M+Na] ⁺ 381.9 [M-H] ⁻ 357.7 [M+Cl] ⁻ 393.8	POS: 179.8(100)/145.9(26)/128.0(22) NEG: 195.6(100)
13.3	62	[M+H] ⁺ 295.6 [M-H] ⁻ 293.7	
13.7	40S	[M+H] ⁺ 359.8 [M+Na] ⁺ 381.8 [M-H] ⁻ 357.7 [M+Cl] ⁻ 393.7	POS: 341.8(15)/197.8(33)/179.9(100)/154.1(11)/146.9(27)/128.0(13) NEG: 195.6(100)
14.7	66	[M+H] ⁺ 399.8 [M-H] ⁻ 397.7 [M+Cl] ⁻ 433.8	POS: 366.9(37)/237.8(100)/169.9(42)122.1(10)/120.0(10) NEG: 235.6(100)/171.8(19)
15.3	101	[M+H] ⁺ 307.8 [M+Na] ⁺ 329.8 [M-H] ⁻ 305.8 [2M-H] ⁻ 612.8	POS: 220.8(31)/218.8(65)/202.8(65)/200.8(49)/184.8(100)/170.0(15)/151.9(42) NEG: 194.7(100)
15.7	11	[M+H] ⁺ 329.9 [M-H] ⁻ 327.7 [M+Cl] ⁻ 363.8	POS: 167.9(100) NEG: 165.7(100)
16.0	84	[M+H] ⁺ 341.8 [M-H] ⁻ 339.7 [M+Cl] ⁻ 375.7 [2M-H] ⁻ 681.0	POS: 179.9(100)/161.9(14)/132.1(35)/114.1(16) NEG: 194.7(22)/177.6(100)/118.9(11)
17.3	46	[M+H] ⁺ 359.6 [M-H] ⁻ 357.7 [M+Cl] ⁻ 393.6	POS: 197.8(100)/121.1(39) NEG: 195.7(100)
17.6	43	[M+H] ⁺ 368.8 [M-H] ⁻ 366.7 [M+Cl] ⁻ 402.7	POS: 206.9(100)/173.8(63)/172.1(16)/161.9(15)/130.0(63) NEG: 204.6(100)/195.5(41)
18.3	69	[M+H] ⁺ 413.8 [M-H] ⁻ 411.8 [M+Cl] ⁻ 447.8	POS: 380.9(18)/379.8(14)/317.7(14)/251.8(100)/201.9(19)/183.9(11)/138.0(17)/134.0(15) NEG: 249.7(100)/185.7(25)

19.9	80	[M+H] ⁺ 429.9 [M-H] ⁻ 427.8 [M+Cl] ⁻ 463.8	POS: 267.8(100) NEG: 265.6(100)
20.2	48	[M+H] ⁺ 398.9 [M-H] ⁻ 396.8	POS: 236.9(95)/160.1(100) NEG: 234.7(100)/194.7(17)
20.4	94	[M+H] ⁺ 355.8 [M-H] ⁻ 353.8 [M+Cl] ⁻ 389.7 [2M-H] ⁻ 708.9	POS: 193.9(100)/175.9(45)/120.1(20) NEG: 191.7(100)
20.5	105	[M+H] ⁺ 343.8 [M-H] ⁻ 341.7 [M+Cl] ⁻ 377.8 [2M-H] ⁻ 684.5	POS: 181.8(100)/103.1(15) NEG: 179.7(100)
22.1	68	[M+H] ⁺ 427.9 [M-H] ⁻ 425.8 [M+Cl] ⁻ 461.8	POS: 395.0(25)/376.8(16)/342.8(26)/265.8(100)/216.9(19)/198.0(18)/196.7(14)/148.1(21) NEG: 263.7(100)/199.8(27)
24.0	79	[M+H] ⁺ 443.9 [M-H] ⁻ 441.8 [M+Cl] ⁻ 477.8	POS: 281.9(100) NEG: 279.6(100)
24.8	47	[M+H] ⁺ 398.8 [M+Na] ⁺ 420.9 [M-H] ⁻ 396.7 [M+Cl] ⁻ 432.8	POS: 236.8(100)/176.8(26)/143.9(67)/130.0(92) NEG: 234.6(100)/204.6(49)/203.5(10)
25.2	[10]	[M+H] ⁺ 401.8 [M-H] ⁻ 399.6 [M+Cl] ⁻ 435.5	POS: 239.8(100)/118.1(38) NEG: 237.6(100)/194.6(13)
25.8	65	[M+H] ⁺ 441.9 [M-H] ⁻ 439.8 [M+Cl] ⁻ 475.8	POS: 407.7(11)/279.8(100)/230.0(19)/211.9(34)/166.1(22)/164.1(12) NEG: 277.7(100)/213.8(18)
28.1	77	[M+H] ⁺ 457.9 [2M+H] ⁺ 937.1 [M-H] ⁻ 455.7 [M+Cl] ⁻ 491.8	POS: 295.9(100) NEG: 293.7(100)

28.2	5	[M+H] ⁺ 415.8 [M-H] ⁻ 413.7 [M+Cl] ⁻ 449.8 [2M-H] ⁻	POS: 253.8(95)/132.0(100)
30.1	87	[M+H] ⁺ 383.9 [M-H] ⁻ 381.8 [M+Cl] ⁻ 417.8 [2M-H] ⁻ 765.0	POS: 221.8(100)/124.1(59) NEG: 261.3(100)/219.8(22)/194.7(22)
31.5	117	[M+H] ⁺ 429.9 [M+Na] ⁺ 451.9 [M-H] ⁻ 427.8 [M+Cl] ⁻ 463.8	POS: 409.9(17)/396.9(53)/362.9(82)/280.9(36)/274.7(17)/267.8(51)/230.9(45)/216.9(14)/174.8(100)/146.0(24)/143.9(17) NEG: 265.6(100)
34.7	92	[M+H] ⁺ 397.8 [M-H] ⁻ 395.8 [M+Cl] ⁻ 431.8 [2M-H] ⁻ 793.1	POS: 235.9(100)/138.1(20) NEG: 233.6(100)

Retention times (Rt). Blažević number (No). Glucosinolates partially characterized with reasonable evidence for one single structure to be naturally biosynthesized in plants [in brackets].