Table S1 Method optimization for quantification of secondary metabolites

Secondary metabolites	Ion mode				Extraction solvents		
	Positive		Negative		Ethanol (peak area)	Methanol (peak area)	70% methanol (peak area)
	Ion pairs	abundance	Ion pairs	abundance			
Gallic acid	-a	-a	169.0→125.0	43290	1081	14414	16916
Proanthocyanidin B1	579.2→73.0	40589	577.1→407.0	16084	26621	77828	74614
Catechin	291.1→139..1	33504	289.1→245.1	134961	130703	190111	179497
Proanthocyanidin B2	579.2→73.1	32829	577.1→407.0	53145	10451	13187	12183
Epicatechin	291.1→139.1	336451	289.1→245.1	46459	5436	8304	7496
cis-THSG	-b	-b	-b	-b	100538	106339	112458
Epcatechini-3-gallate	443.1→123.0	108037	441.1→169.0	158778	803693	205802	789209
trans-THSG	407.1→245.1	971191	405.0→243.0	778569	15209041	16725440	17105686
Emodin-8-*O*-β-D-glucoside	433.1→365.1	856	431.1→269.1	835457	2810316	2576490	3197349
Physcion-8-*O*-β-D-glucoside	447.1→207.1.1	13145	445.1→283.1	26439	54205	36351	62959
Emodin	271.1→115.0	15371	269.0→225.0	255952	366282	504696	559892
Physcion	285.1→139.0	35857	283.0→240.0	17876	30143	36044	61706
total	-	1587830	-	2367010	19548507	20495004	22179962

Data in the table is an average of duplicate. a) No ion pair was found under the positive mode; b) for the ion mode selection, *cis*-THSG was referenced with its isomer *trans*-THSG.

Table S2 Quantitative results of secondary metabolites in raw materials of PMR (μg·g^{-1}) (n=3)

Secondary metabolites	Mean (RSD %)									One-way ANOVA *P* value
	PMR-RMA1	PMR-RMA2	PMR-RMA3	PMR-RMA4	PMR-RMA5	PMR-RMA6	PMR-RMA7	PMR-RMA8	PMR-RMA9	
Gallic acid	402.07(1.80)	186.06(4.06)	182.35(6.37)	253.46(4.44)	179.23(4.98)	166.29(9.04)	227.60(11.04)	162.81(7.98)	197.92(2.10)	0.605
Proanthocyanidin B1	295.02(4.25)	490.67(3.16)	493.72(2.55)	406.08(3.11)	502.83(4.49)	507.67(0.43)	485.89(4.23)	611.76(3.15)	635.29(0.80)	0.173
Catechin	1274.44(1.83)	1740.64(2.05)	1662.55(4.98)	1647.71(0.94)	1689.03(3.20)	1674.20(13.81)	1781.35(9.49)	1959.84(4.14)	2126.65(7.37)	0.076
Proanthocyanidin B2	84.26(7.14)	160.86(5.68)	150.71(1.71)	111.53(6.27)	179.71(6.11)	159.64(0.75)	115.88(9.61)	168.66(5.34)	193.97(2.81)	0.693
Epicatechin	71.56(13.22)	98.09(7.06)	88.80(5.61)	65.12(5.34)	89.49(3.05)	88.93(2.46)	76.48(15.14)	105.27(5.21)	113.88(8.29)	0.438
cis-THSG	684.52(8.66)	870.18(13.59)	772.65(10.00)	759.46(16.08)	847.04(11.74)	828.27(8.72)	685.83(10.79)	781.87(9.23)	901.23(10.12)	0.880
Epcatechini-3-gallate	108.96(5.21)	225.90(1.33)	205.48(3.92)	144.92(3.58)	224.15(1.91)	195.86(1.31)	154.64(6.00)	225.56(3.28)	246.99(2.78)	0.783
trans-THSG	38539.11(2.30)	42967.88(2.63)	44548.99(0.13)	42211.42(2.21)	43487.67(1.24)	42862.64(0.51)	43803.45(4.80)	45470.41(1.22)	47003.93(2.17)	0.188
Emodin-8-*O*-β-D-glucoside	248.69(5.21)	1120.62(1.76)	1159.35(0.36)	582.48(1.06)	1042.90(1.70)	1104.73(1.39)	717.48(0.66)	1206.13(1.26)	1122.51(0.69)	0.852
Physcion-8-*O*-β-D-glucoside	60.26(6.46)	288.31(2.42)	288.16(4.69)	141.12(2.46)	240.22(3.62)	255.17(2.39)	180.54(4.60)	314.43(8.07)	229.08(0.94)	0.907
Emodin	902.99(2.19)	349.57(1.46)	371.48(1.85)	652.66(2.49)	332.25(2.36	312.93(1.54)	653.89(2.05)	302.52(4.31)	309.05(2.65)	0.805
Physcion	597.68(1.39)	313.10(4.98)	334.08(5.86)	445.46(1.33)	307.35(4.92)	278.71(4.23)	452.86(6.71)	318.08(11.01)	310.43(13.22)	0.741

Data in the table is an average of triplicate, and the numbers in parentheses/brackets are the RSD values in % of triplicate.

Table S3 Quantitative results of secondary metabolites in micro-dissected tissues of PMR (ng/10^6 μm^2) (n=3)

Secondary metabolites	micro-dissected tissues	Mean (RSD %)								
		PMR-TA1	PMR-TA2	PMR-TA3	PMR-TB1	PMR-TB2	PMR-TB3	PMR-TC1	PMR-TC2	PMR-TC3
gallic acid	CR	110.97(3.66)	97.42(4.09)	121.34(6.40)	75.63(11.43)	213.00(3.65)	120.30(6.63)	48.82(6.87)	63.04(10.95)	62.98(1.98)
	CT	39.94(4.26)	83.67(1.20)	83.27(11.17)	30.67(14.86)	33.25(13.72)	86.27(1.51)	26.29(5.08)	31.69(2.84)	32.46(3.64)
	XAB	7.73(9.35)	9.28(10.57)	7.69(14.37)	9.16(4.16)	9.16(18.05)	6.51(22.77)	12.57(3.44)	14.69(2.31)	9.86(2.07)
	PAB	8.01(18.61)	6.39(6.11)	9.39(14.20)	9.11(8.47)	10.88(11.11)	15.40(13.54)	14.47(6.45)	17.48(2.63)	10.23(2.62)
	X	10.13(3.25)	6.88(1.20)	6.14(8.08)	10.68(7.11)	15.65(7.70)	8.18(27.13)	15.95(16.12)	12.68(2.37)	7.37(11.28)
	P	13.95(3.43)	7.84(6.43)	7.82(10.52)	8.58(1.87)	16.44(2.66)	9.51(12.34)	12.37(2.93)	12.49(2.16)	8.82(21.04)
proanthocyanidin B1	CR	57.23(0.92)	35.49(2.20)	54.25(8.59)	19.11(16.34)	49.64(5.42)	11.25(1.94)	9.86(3.06)	18.43(2.44)	37.27(7.45)
	CT	6.66(6.28)	9.14(2.95)	14.74(9.87)	6.21(9.77)	9.14(20.65)	3.34(10.99)	3.62(10.94)	4.92(10.99)	6.27(2.12)
	XAB	4.82(4.16)	4.78(6.07)	6.26(6.35)	1.52(18.30)	2.28(6.38)	1.74(34.18)	2.41(3.15)	3.06(17.79)	7.02(0.61)
	PAB	4.27(24.19)	4.89(2.86)	6.35(5.69)	1.34(17.23)	2.15(9.37)	3.66(7.88)	2.39(9.35)	2.39(14.75)	5.98(5.59)
	X	4.18(17.36)	3.86(5.70)	6.46(9.45)	1.76(12.11)	2.66(15.73)	1.89(11.41)	2.38(19.70)	3.23(3.27)	6.11(16.74)
	P	4.66(5.33)	4.83(8.28)	7.58(8.13)	1.28(18.82)	2.59(6.54)	1.75(17.69)	3.41(5.48)	3.48(1.15)	5.90(6.04)
catechin	CR	180.76(2.13)	101.37(2.87)	186.85(7.00)	147.70(8.00)	287.19(2.66)	43.10(7.18)	21.23(5.45)	48.75(4.96)	71.46(3.73)
	CT	15.67(9.78)	29.40(1.18)	44.19(6.65)	78.38(3.87)	54.06(15.52)	22.46(1.99)	4.62(4.25)	10.27(9.46)	9.24(8.09)
	XAB	22.36(10.71)	38.57(4.02)	35.98(3.01)	23.29(8.05)	31.01(7.92)	22.26(9.54)	6.11(3.27)	11.11(8.54)	17.90(2.26)
	PAB	21.60(17.15)	34.44(4.30)	40.69(7.84)	25.31(2.73)	20.60(86.86)	35.83(6.87)	6.39(5.01)	8.59(8.50)	15.13(3.57)
	X	20.97(6.61)	25.16(7.30)	27.60(8.05)	39.92(5.84)	36.35(6.76)	20.64(8.95)	7.66(2.50)	8.67(5.15)	22.62(10.25)
	P	24.26(3.80)	31.81(5.30)	32.55(3.85)	34.56(6.07)	36.79(4.07)	17.67(9.32)	7.98(7.18)	8.56(6.90)	18.19(7.18)
proanthocyanidin B2	CR	5.57(7.90)	4.82(7.20)	4.40(12.10)	1.97(22.50)	3.75(10.65)	1.96(16.05)	9.87(4.24)	12.11(4.01)	12.68(7.86)

	CT	1.87(13.37)	4.57(4.51)	3.53(4.67)	1.78(7.66)	1.43(8.90)	1.55(9.93)	8.02(7.53)	9.85(6.45)	6.24(3.29)
	XAB	1.70(15.29)	2.65(14.18)	1.87(11.19)	*	*	0.81(19.84)	7.31(4.88)	4.66(15.15)	5.70(4.65)
	PAB	1.98(10.10)	2.81(7.02)	1.85(5.05)	1.49(12.04)	*	*	7.44(20.66)	4.15(7.73)	6.50(10.63)
	X	1.51(16.56)	2.47(13.27)	1.66(10.38)	*	*	*	7.54(11.86)	5.48(10.39)	11.69(14.65)
	P	1.63(21.47)	2.32(5.07)	1.38(24.65)	*	0.81(10.43)	*	9.21(5.29)	6.71(8.45)	13.09(7.83)
epicatechin	CR	13.49(1.88)	14.22(6.55)	14.23(4.86)	3.10(17.42)	9.37(7.36)	3.54(7.86)	7.65(5.10)	17.30(6.59)	35.48(5.74)
	CT	1.75(19.05)	3.65(8.46)	4.24(8.42)	*	*	*	3.83(15.57)	4.32(3.49)	10.05(8.04)
	XAB	2.60(9.18)	2.74(17.79)	*	*	*	*	4.29(6.79)	3.75(5.36)	13.73(2.55)
	PAB	2.35(4.48)	2.12(11.01)	3.16(9.52)	*	*	1.90(5.95)	4.18(8.46)	3.65(5.45)	12.15(5.11)
	X	2.01(2.73)	*	1.77(3.32)	*	*	*	4.59(8.87)	5.01(0.81)	17.05(13.84)
	P	2.49(15.33)	2.54(23.02)	2.45(18.77)	*	*	*	4.69(5.71)	4.70(8.84)	13.76(10.53)
***cis*-THSG**	CR	189.76(4.08)	123.52(6.57)	157.43(6.20)	244.08(5.52)	304.24(3.33)	123.34(3.20)	116.48(6.11)	180.27(6.01)	102.23(11.45)
	CT	85.39(4.34)	103.89(2.67)	199.38(7.13)	160.94(8.80)	133.03(10.09)	152.86(1.35)	154.82(2.19)	192.25(7.27)	65.39(1.60)
	XAB	128.35(6.52)	135.58(0.65)	133.87(6.70)	105.94(16.36)	155.29(5.71)	116.16(3.90)	183.62(3.74)	218.33(1.52)	108.47(2.17)
	PAB	132.48(11.93)	140.21(5.58)	168.02(4.38)	105.53(12.99)	150.38(13.10)	158.59(6.77)	190.32(8.24)	216.64(2.55)	78.09(0.86)
	X	136.10(5.57)	157.74(3.50)	183.04(4.59)	125.80(6.58)	167.50(3.53)	119.39(8.87)	199.40(2.51)	239.20(1.19)	131.07(15.63)
	P	153.33(5.04)	192.25(2.53)	227.34(1.85)	131.90(1.83)	168.83(2.04)	101.65(13.51)	207.53(1.92)	243.56(1.09)	117.72(2.02)
epicatechin-3-gallate	CR	2.81(7.74)	3.99(4.31)	3.18(14.24)	2.83(12.28)	6.36(3.31)	0.66(14.24)	5.16(2.99)	10.01(6.74)	17.26(1.90)
	CT	1.12(10.63)	4.00(2.11)	1.38(20.97)	2.26(10.92)	1.07(10.66)	0.69(24.35)	6.76(2.51)	8.69(10.74)	14.68(4.44)
	XAB	1.69(9.66)	4.93(14.68)	1.56(10.58)	3.30(16.39)	0.70(18.50)	0.75(13.36)	12.47(6.99)	8.94(7.87)	40.08(1.71)
	PAB	2.06(24.08)	3.87(7.75)	1.36(6.90)	2.70(25.19)	0.84(31.40)	1.74(5.14)	14.01(14.96)	8.55(10.13)	34.56(2.58)
	X	1.78(15.29)	3.20(1.17)	1.72(13.88)	2.56(3.51)	0.87(4.60)	0.71(16.40)	15.88(8.07)	8.68(4.22)	31.38(9.42)
	P	1.97(5.23)	4.39(8.03)	1.35(19.26)	1.89(14.24)	0.57(18.43)	0.50(10.38)	17.56(11.11)	10.59(11.52)	26.65(7.45)

***trans*-THSG**	CR	898.54(1.72)	621.95(13.99)	522.94(3.82)	1242.26(7.65)	1271.63(1.58)	499.75(3.10)	528.15(5.20)	936.45(7.57)	457.52(4.41)
	CT	255.06(2.76)	262.00(15.07)	421.98(10.50)	387.70(8.68)	453.24(10.77)	349.04(0.27)	406.06(4.85)	616.05(13.46)	133.58(1.11)
	XAB	154.51(5.57)	143.40(4.25)	165.36(7.57)	132.83(9.35)	225.86(8.57)	155.85(12.88)	348.95(6.08)	339.33(2.10)	126.00(0.79)
	PAB	157.59(9.55)	152.16(7.60)	200.27(12.70)	165.02(2.68)	199.77(16.45)	98.94(8.57)	273.09(8.57)	378.08(3.71)	87.88(2.98)
	X	163.41(13.00)	167.40(5.00)	336.13(9.46)	117.43(7.66)	285.47(9.88)	167.65(11.12)	300.80(6.64)	603.67(6.46)	171.76(1.40)
	P	236.61(5.51)	187.20(7.74)	291.68(6.64)	90.80(13.65)	322.83(1.40)	125.64(10.13)	348.36(3.31)	462.93(0.19)	153.76(3.31)
emodin-8-*O*-β-D-glucoside	CR	0.55(7.27)	1.47(8.00)	0.20(7.15)	1.58(4.03)	1.59(7.88)	1.34(3.18)	5.68(9.33)	5.54(3.10)	1.82(3.15)
	CT	0.27(7.41)	0.73(6.56)	0.17(11.02)	0.50(20.63)	0.28(12.37)	0.83(1.99)	2.93(9.80)	3.62(7.33)	0.46(3.24)
	XAB	0.19(10.53)	0.08(12.20)	0.11(6.40)	0.15(17.08)	0.14(3.70)	*	0.36(19.34)	0.25(12.60)	0.09(6.26)
	PAB	0.09(11.11)	0.05(18.15)	0.08(16.97)	0.11(26.61)	0.14(20.33)	0.16(13.09)	0.18(9.53)	0.34(3.07)	0.06(13.96)
	X	0.14(21.43)	0.13(4.48)	0.18(10.47)	0.12(11.15)	0.09(12.96)	*	0.14(11.49)	0.31(2.02)	0.12(8.84)
	P	0.05(20.00)	0.05(23.50)	0.12(11.27)	0.06(14.01)	0.09(2.06)	*	0.04(9.51)	0.32(12.67)	0.05(16.29)
physcion-8-*O*-β-D-glucoside	CR	5.52(16.54)	2.07(11.07)	7.86(2.59)	13.97(4.87)	3.75(2.22)	1.54(5.07)	1.26(23.62)	2.67(10.81)	2.67(6.74)
	CT	3.36(13.13)	1.92(7.45)	3.01(2.63)	7.30(4.86)	2.90(2.13)	0.24(25.57)	*	0.45(10.10)	1.86(6.05)
	XAB	1.46(9.15)	0.59(20.54)	0.58(14.47)	0.30(8.45)	0.36(24.66)	0.06(23.86)	*	*	*
	PAB	1.37(14.24)	0.08(33.03)	0.38(23.23)	0.22(15.74)	0.23(9.86)	*	*	*	*
	X	0.82(15.15)	0.28(13.96)	0.28(12.33)	0.17(22.86)	0.45(4.44)	0.11(24.70)	*	*	*
	P	0.22(13.03)	*	0.15(8.60)	*	0.23(31.40)	*	*	*	*
emodin	CR	13.84(9.39)	13.86(8.92)	10.99(6.23)	3.81(9.68)	1.21(8.80)	11.86(12.13)	5.95(7.15)	14.49(.63)	11.47(8.16)
	CT	8.57(4.57)	12.00(1.29)	11.71(5.33)	3.13(21.58)	5.08(8.73)	12.82(2.17)	4.85(11.62)	12.70(7.04)	9.32(2.50)
	XAB	14.07(8.46)	10.38(3.49)	26.45(2.03)	5.45(12.50)	5.45(15.98)	9.15(5.00)	40.75(9.61)	48.21(8.84)	8.05(1.96)
	PAB	3.95(18.15)	3.25(8.54)	3.89(13.00)	0.68(24.60)	1.33(32.58)	7.68(6.26)	6.38(4.50)	6.38(12.87)	6.03(0.63)
	X	14.40(6.39)	13.92(4.74)	23.53(3.98)	7.11(4.56)	2.25(21.42)	8.22(10.00)	8.12(3.28)	30.11(13.88)	8.98(5.27)

	P	2.75(13.72)	3.56(13.25)	5.67(6.01)	0.83(15.79)	0.62(9.63)	2.02(10.20)	5.62(16.56)	2.97(2.68)	5.64(3.39)
physcion	CR	4.72(14.36)	6.18(12.13)	2.94(14.16)	2.04(4.55)	1.25(11.52)	5.11(19.60)	1.57(11.98)	3.14(12.76)	2.40(4.80)
	CT	2.46(7.55)	5.20(6.39)	3.80(13.01)	1.64(18.98)	2.31(24.48)	7.04(4.77)	1.26(5.25)	2.85(4.86)	2.28(3.89)
	XAB	9.03(7.29)	6.44(11.80)	14.53(15.96)	2.10(12.86)	3.33(18.90)	4.80(11.51)	14.82(3.87)	16.84(12.97)	1.97(3.68)
	PAB	0.78(25.83)	1.00(1.59)	0.94(26.94)	0.76(11.41)	0.83(28.51)	1.93(13.06)	1.22(1.63)	1.52(3.77)	1.66(6.76)
	X	8.14(10.63)	6.61(8.18)	17.21(1.56)	3.86(9.08)	1.27(24.62)	3.38(8.78)	1.85(3.35)	17.83(9.79)	2.62(4.43)
	P	0.98(15.93)	0.88(27.62)	1.65(6.78)	0.88(24.32)	0.90(8.10)	1.02(8.72)	1.26(9.19)	1.11(5.31)	1.48(8.95)

Data in the table is an average of triplicate, and the numbers in parentheses/brackets are the RSD values in % of triplicate; * represent undetected.