

SUPPLEMENTARY MATERIALS

The supplementary figures and tables are provided as additional information to support the main results reported in this study. All the experimental raw data, figures and tables that are not included in this manuscript are available from the corresponding author, Dr Fidele Tugizimana, Department of Biochemistry at the University of Johannesburg.

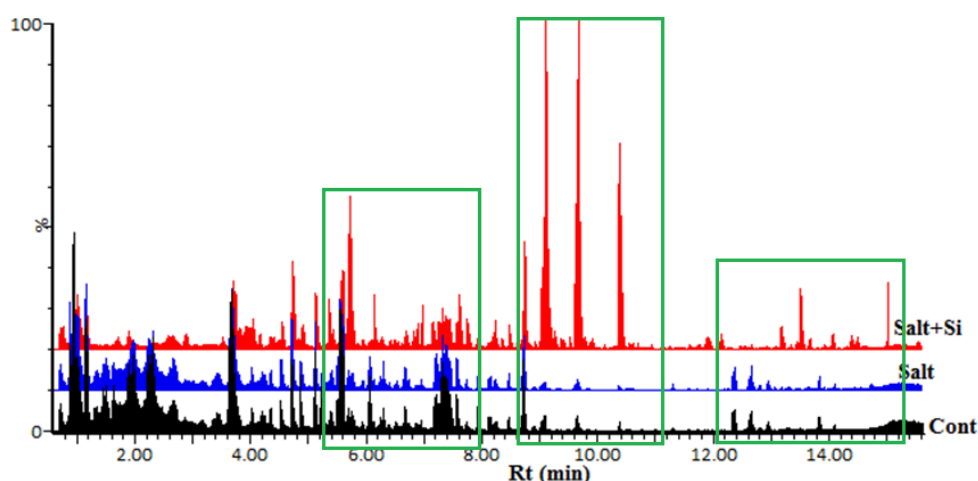


Figure S1: Representative UHPLC-MS BPI chromatograms from the ESI negative data showing treatment-related metabolic variations. The overlaid chromatograms display several ion peaks reflective of the complexity of the biological leaf extracts from non-stressed controls (black), naïve salt-stressed samples (blue), and silicon-treated salt-stressed samples (red). Visual inspection of the highlighted regions on the chromatograms shows differential peak intensities between the treatments, as well as the absence and presence of some peaks.

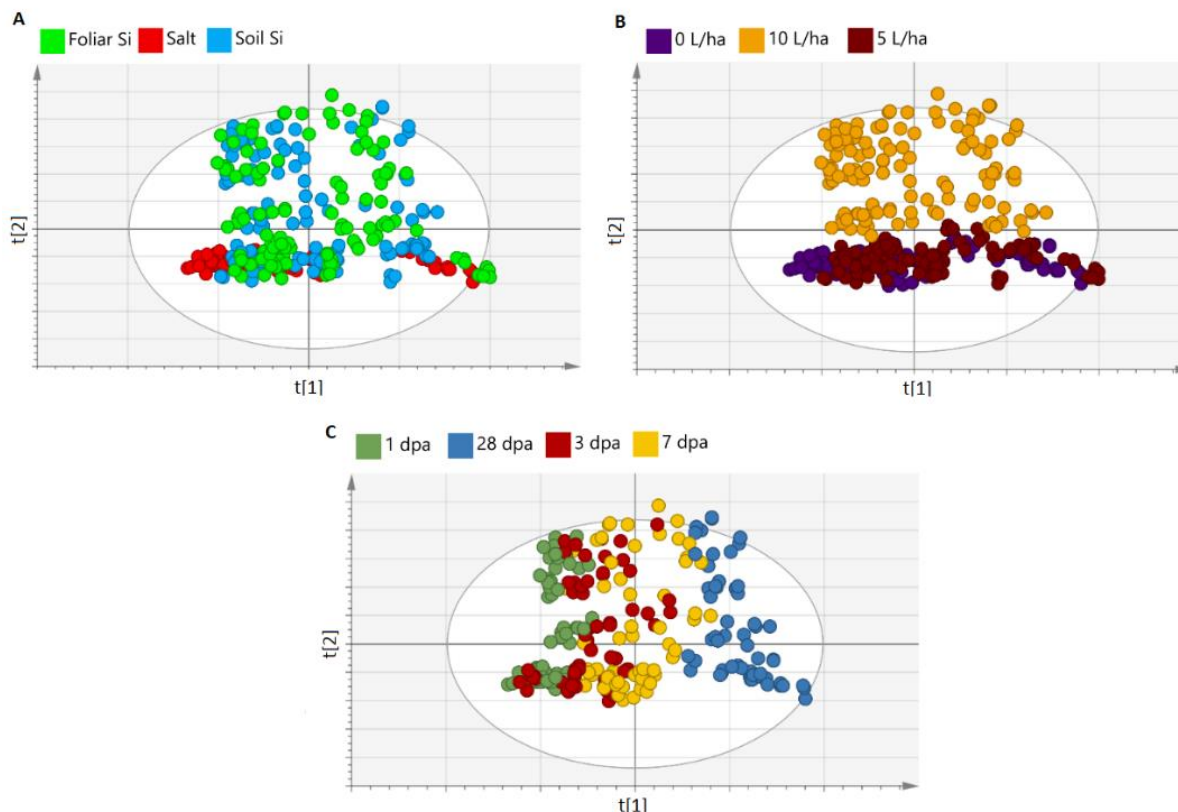


Figure S2: Unsupervised machine learning (ML)-based chemometric modelling of the ESI negative data – principal component analysis (PCA) scores plots. The PCA scores plots provide a visual overview of the multi-dimensional data, allowing identification of natural treatment-related sample groupings and patterns. The 18-component PCA model computed from the Pareto-scaled data exhibit 0.802 explained variation (R^2) and 0.653 predicted variation (Q^2), according to the 7-fold cross validation. Visual inspection reveals that silicon treatment of salt-stressed samples has an effect regardless of area of application (A), concentration of Si-based formulation (B) and a time points investigated (C).

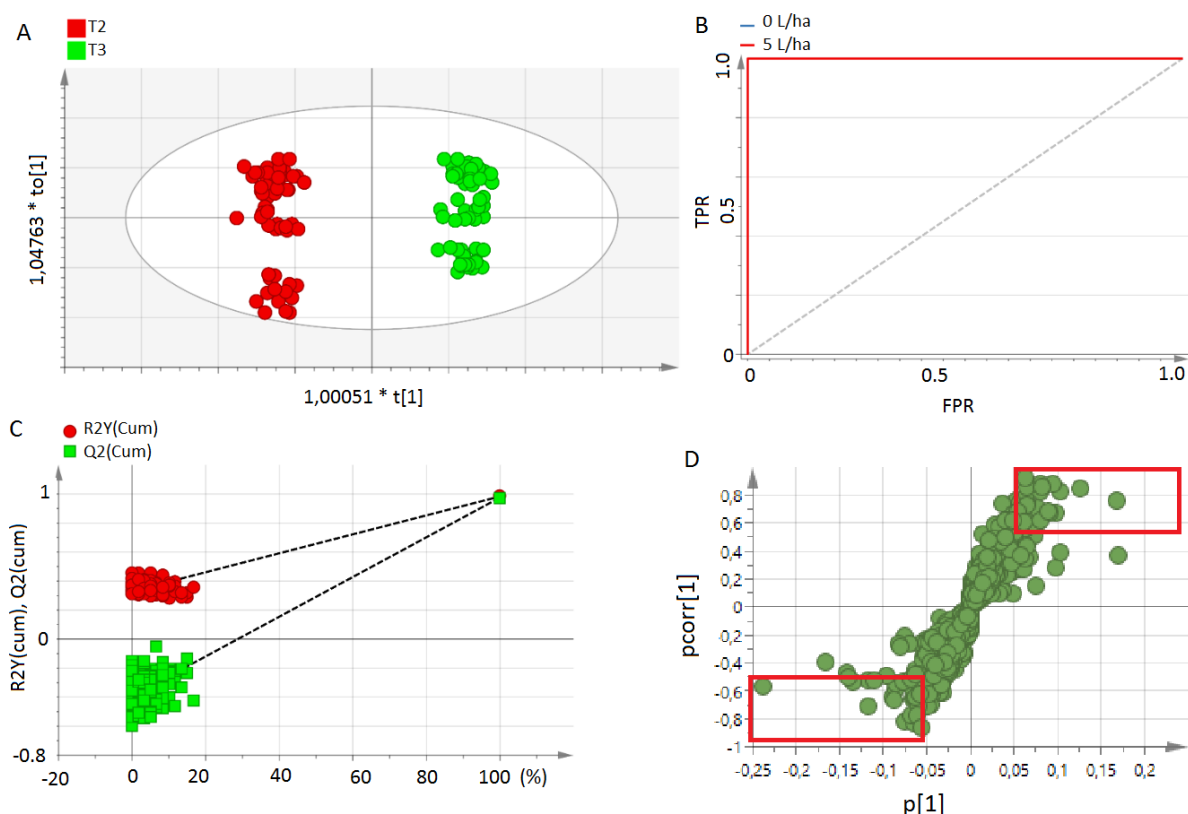


Figure S3: Representation of supervised machine learning (ML)-based orthogonal projection of latent structures discriminant analysis (OPLS-DA) modelling of the data. This supervised regression provided a visual and supervised classification of the data groups and permits extraction of statistically significant metabolites in the discrimination of naïve salt-stressed samples (T2 - red) and the biostimulant-treated salt-stressed samples (T3 - green), as presented on the OPLS-DA scores plot (A). The model was validated by assessing its robustness (B: receiver operator characteristic (ROC) curves), predictive ability and reliability (C: permutation test), and its significance using cross-validated analysis of variance (CV-ANOVA) tests. The scrutinised models were found to be very good classifiers with 100% sensitivity and 100% specificity (B), and none of the permuted models were found to have better performance than the selected ones (C), with cumulative R^2Y and $Q^2 > 0.95$ (0.983 and 0.976, respectively in the presented model), and reliable statistical significance (CV-ANOVA: p -value < 0.05). The constructed OPLS-DA loadings S-plot (D) was used to identify statistically significant metabolites/variables with both high correlation and covariance, as indicated on the figure (red) rectangles.

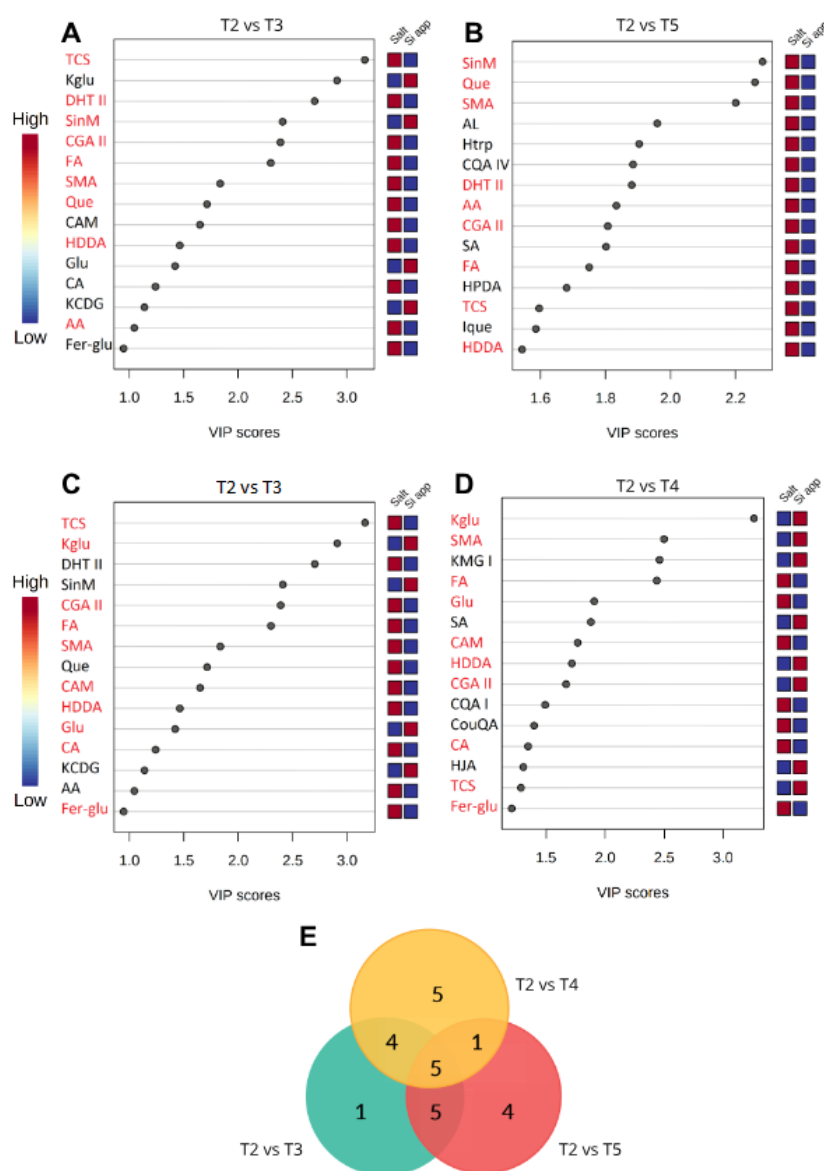


Figure S4: Identification of the statistically significant features/metabolites in different treatments discriminations using the variable importance in projections (VIP) plots. Important metabolites in the discriminations between treatments were identified using VIP computations (in accordance with the OPLD-DA S-loadings plot, the higher the VIP score (>1), the more significant the metabolite in the classification). The plots were used to investigate the effect of silicon-treatment on salt-stressed plants based on formulation concentration: **A** (5 L/ha soil applied Si-based biostimulant) vs. **B** (10 L/ha soil applied Si), and on Si-application area **C** (5 L/ha soil applied Si-based biostimulant) vs. **D** (5 L/ha foliar applied Si-based biostimulant). The identified common metabolites between the treatment comparisons were highlighted in red and presented in a Venn diagram (**E**). The 5 L/ha soil applied Si-formulation (T3) exhibits more common metabolites with both the 10 L/ha soil applied Si-based biostimulant and the 5 L/ha foliar applied Si-based biostimulant.

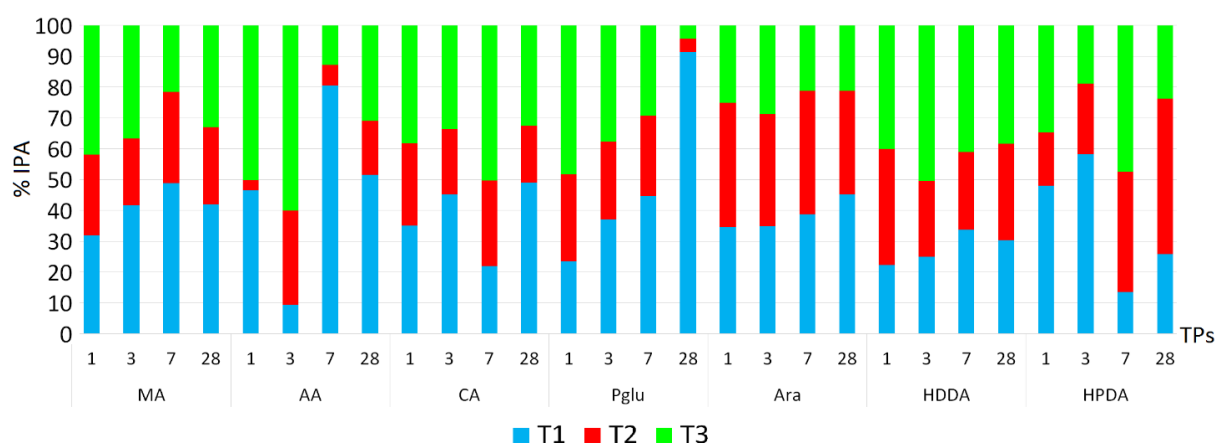
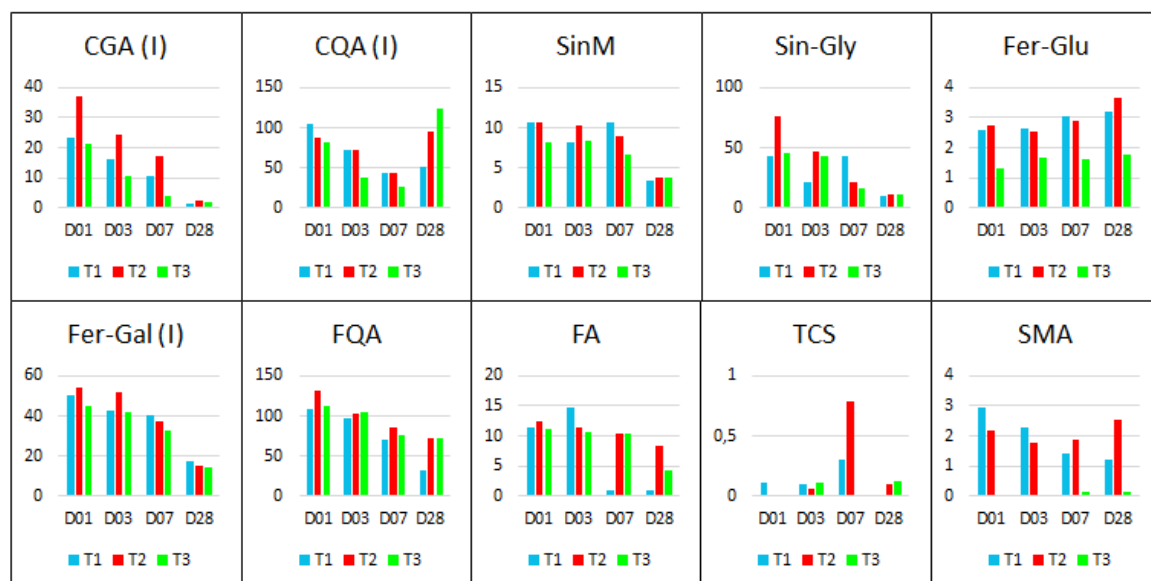


Figure S5: Summarised effects of silicon treatment of salt-stressed plants on detected primary metabolism components of organic acids (MA, AA, CA), sugars (Pglu, Ara) and fatty acids (HDDA, HPDA). The constructed stacked column graphs display relative integrated peak area percentages (% IPA) of metabolites across non-stress- (T1, blue), naïve salt stress- (T2, red) and biostimulant treated salt stress (T3, green) conditions across all time points (days 1, 3, and 28). **Abbreviations:** MA, malic acid; AA, ascorbic acid; CA, citric acid; Pglu, phosphogluconate; Ara, arabinose; HDDA, hexadecadienoic acid; HPDA, hydroperoxyoctadecadienoic acid.

A



B

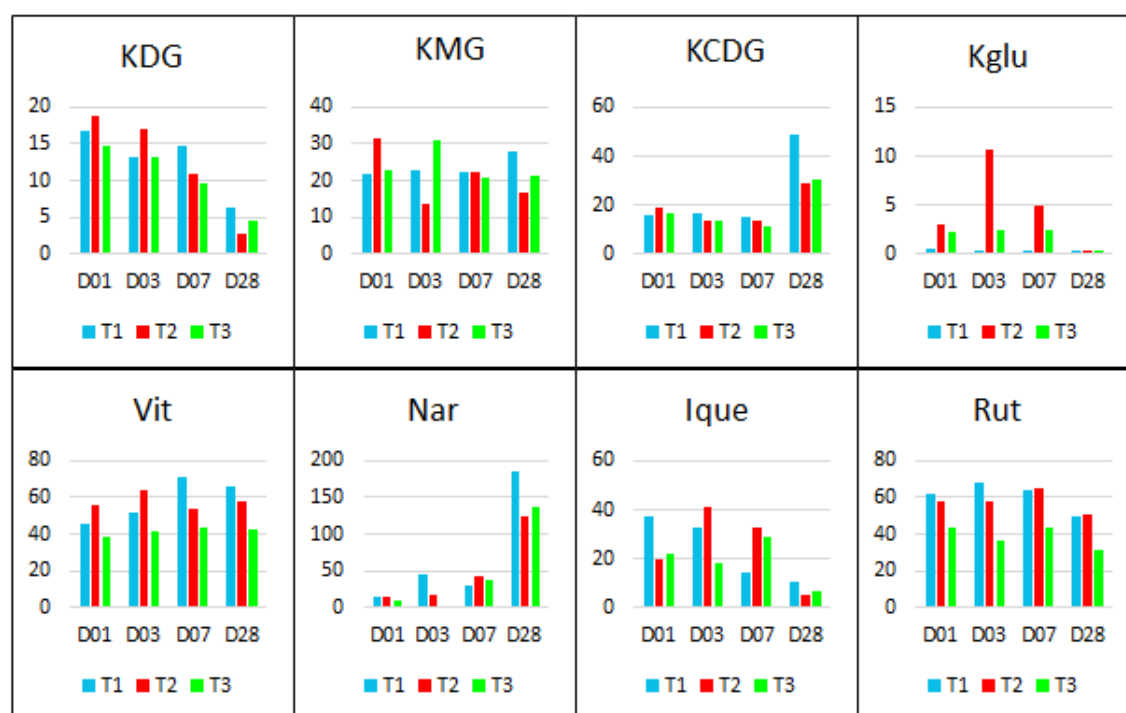


Figure S6: An overview of relative phenolics and polyamine content fluctuations in different treatments. The column graphs were constructed based on integrated peak areas (IPA) of pure and/or conjugated phenolic acids and polyamines (A) and flavonoids (B) in non-stress- (T1, blue), naïve salt stress- (T2, red), and biostimulant treated salt stress (T3, green) conditions across all time points (days 1, 3, and 28). **Abbreviations:** CouQA, coumaroyl-quinic acid; CouGA, coumaroyl-galactarate; CQA, caffeoyl-quinic acid; CGA, caffeoyl-galactarate; FA, ferulic acid; FQA, feruloyl-quinic acid; Fer-glu, feruloyl-glucoside; Sin-Gly, sinapoyl-glycoside; SinM, sinapoyl-malate; TCS, tricoumaroyl-spermidine; SMA, spermidine monoaldehyde; Que, quercetin; Qtrn, quercetrin; Ique, isoquercetin; Kglu, kaempferol glucoside; KCDG, kaempferol coumaroyl-diglucosyl-glucoside; KMG, kaempferol malonoyl-glucoside; KDG, kaempferol diglucosyl-glucoside; Vit, vitexin; Nar, naringin; Rut, rutin.

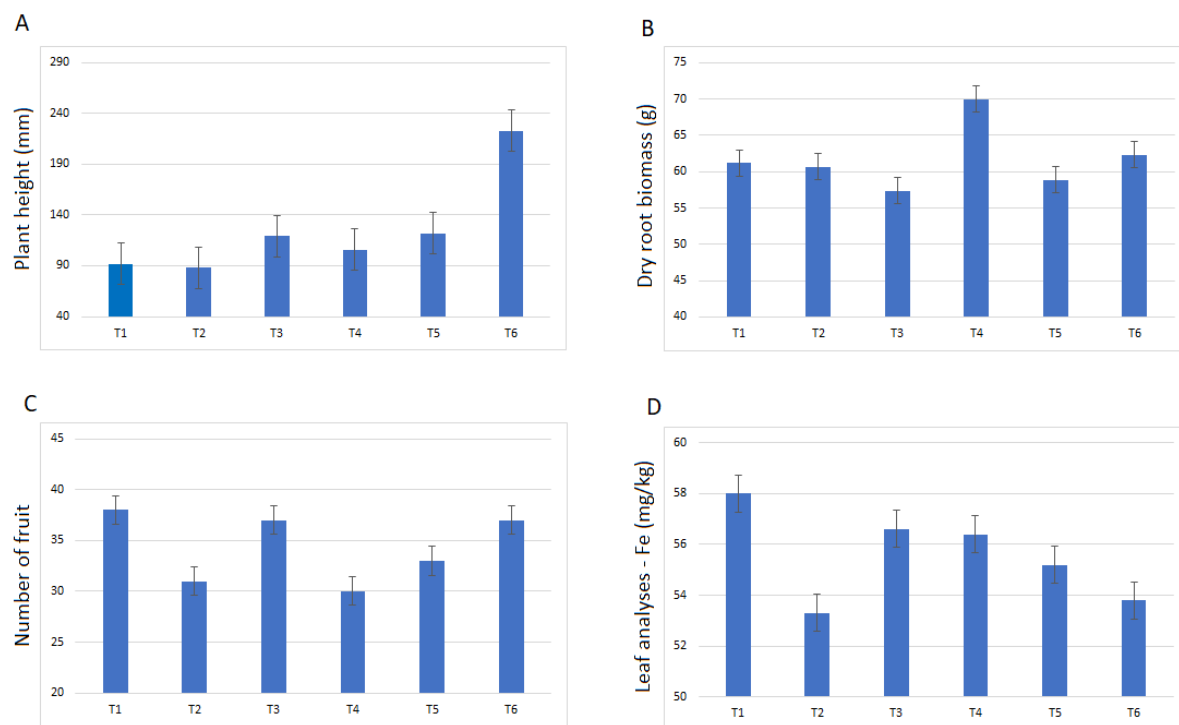


Figure S7: The effects of different treatments on the agronomic and phenotypic states of the plant samples. The graphs present general increases in plant height (A), dry root biomass (B), number of fruits (C), and leaf analyses of iron content (D) induced by Si treatment of the salt stressed plants (T2) at both foliar (T4 and T6) and soil (T3 and T5) applied biostimulant.

Table S1. Metamapp data used for generation of a network (Figure 4).

PubChem_ID	KEGG_ID	SMILES	Compound_Name	Salt stress effect		Si biostimulant effect	
				Fold change	p-value	Fold change	p-value
699414	C01494	<chem>COC1=CC=C(C=C1)C=CC(=O)O</chem>	4-Methoxycinnamic acid	1.00E+00	5.00E-02	1.00E+00	5.00E-02
70912	C02710	<chem>CC(C)CC(C(=O)O)NC(=O)C</chem>	Acetyl leucine	9.17E-01	7.05E-01	6.52E-02	1.20E-06
700653	C03137	<chem>CC(=O)NC(CC1=CNC2=CC=CC=C21)C(=O)O</chem>	Acetyl tryptophan	6.76E-01	1.56E-01	1.54E+00	9.15E-02
5484352	C00041	<chem>CC(C(=O)O)NC(C(=O)O)N</chem>	Alanyl alanine	1.01E+00	5.00E-02	1.00E+02	2.05E-03
16950	C03406	<chem>C(CC(C(=O)O)N)CN=C(N)NC(CC(=O)O)C(=O)O</chem>	Argininosuccinate	1.01E+00	5.00E-02	1.00E+00	5.00E-02
54670067	C00072	<chem>C(C(C1C(=C(C(=O)O1)O)O)O)O</chem>	Ascorbic acid	6.13E-02	3.72E-02	9.15E-01	9.35E-01
5459979	C03062	<chem>C1=CC(=C(C=C1C=CC(=O)OC(C(C(C(=O)O)O)O)O)C(=O)O)O)O</chem>	Caffeoylgucaric acid	1.17E+05	3.26E-01	2.66E-01	2.05E-04
5281761	C10433	<chem>C1=CC(=C(C=C1C=CC(=O)OC2C(C(C(C(=O)O)O)O)O)O)O</chem>	Caffeoylglycoside	4.76E+04	1.22E-04	7.47E-01	1.95E-01
10155076	C00852	<chem>C1C(C(C(CC1(C(=O)O)OC(=O)C=CC2=CC(=C(C=C2)O)O)O)O)O</chem>	Caffeoylquinic acid	1.35E+05	7.92E-03	8.83E-01	1.00E-01
93072	C00438	<chem>C(C(C(=O)O)NC(=O)N)C(=O)O</chem>	Carbamoylaspartate	1.01E+00	5.00E-02	1.00E+00	5.00E-02
448878	C00073	<chem>CSCCC(C(=O)O)NC(=O)N</chem>	Carbamylmethionine	9.06E-01	7.84E-02	9.30E-01	1.69E-01
12039	C00251	<chem>C=C(C(=O)O)OC1C=C(C=CC1O)C(=O)O</chem>	Chorismic acid	1.01E+00	5.00E-02	1.00E+00	5.00E-02
311	C00158	<chem>C(C(=O)O)C(CC(=O)O)(C(=O)O)O</chem>	Citric acid	1.00E+00	5.00E-02	1.00E+00	5.00E-02
6440013	C00223	<chem>CC(C)(COP(=O)(O)OP(=O)(O)OCC1C(C(C(O1)N2C=NC3=C(N=CN=C32)N)O)OP(=O)(O)O)C(C(=O)NCCC(=O)NCCSC(=O)C=CC4=CC=C(C=C4)O)O</chem>	Coumaroylgucaric acid	9.22E-01	5.80E-01	2.78E-01	7.60E-05
14158103	C12208	<chem>C1C(C(C(CC1(C(=O)O)O)OC(=O)C=CC2=CC=C(C=C2)O)O)O</chem>	Coumaroylquinic acid	9.12E-01	5.58E-01	6.83E-01	1.65E-02
6251	C00392	<chem>C(C(C(C(C(CO)O)O)O)O)O</chem>	D-mannitol	1.00E+00	5.00E-02	1.00E+00	5.00E-02
5281416	C09263	<chem>C1=CC(=O)OC2=CC(=C(C=C21)O)O</chem>	Esculetin	1.00E+00	5.00E-02	1.00E+00	5.00E-02
445858	C01494	<chem>COC1=C(C=CC(=C1)C=CC(=O)O)O</chem>	Ferulic acid	1.00E+02	1.35E-02	1.29E+00	5.94E-01
14104340	C03156	<chem>COC1=C(C=CC(=C1)C=CC(=O)OC(C(C(C(=O)O)O)O)O)C(=O)O)O</chem>	Feruloylgalactarate	8.23E-01	4.55E-03	5.23E-01	1.50E-06
13962928	C17759	<chem>COC1=C(C=CC(=C1)C=CC(=O)OC2C(C(C(C(=O)O)O)O)O)O</chem>	Feruloylglucose	8.88E-01	6.68E-02	8.29E-01	3.75E-04
9799386	C02572	<chem>COC1=C(C=CC(=C1)C=CC(=O)OC2CC(CC(C2O)O)(C(=O)O)O)O</chem>	Feruloylquinic acid	8.16E-01	6.94E-02	7.83E-01	4.00E-02
5273568	C09266	<chem>COC1=C(C(=C2C(=C1)C=CC(=O)O2)OC3C(C(C(C(=O)O)O)O)O)O</chem>	Fraxin	1.00E+00	5.00E-02	1.00E+00	5.00E-02
33037	C00818	<chem>C(C(C(C(=O)O)O)O)(C(C(=O)O)O)O</chem>	Glucaric acid	1.00E+00	5.00E-02	1.00E+00	5.00E-02
4525487	C00302	<chem>C(CC(=O)[O-])C(C(=O)[O-])[NH3+]</chem>	Glutamate	2.03E+05	3.02E-06	1.00E-02	2.66E-16

5287779	C00064	CC(C)(C)OC(=O)C(CCC(=O)N)N	Glutamine butyl ester	2.60E+05	4.49E-01	9.87E+01	3.78E-02
123938	C00669	C(CC(=O)NC(CS)C(=O)O)C(C(=O)O)N	Glutamylcystine	1.00E+00	5.00E-02	1.00E+00	5.00E-02
92843	C02155	CC(C)CC(C(=O)O)NC(=O)CN	Glycylleucine	4.06E+05	2.12E-01	5.10E+00	9.48E-08
13932172	C21980	CCCCC=CCC=CCCCC(=O)O	Hexadecadienoic acid	1.07E+05	4.26E-02	2.21E+01	1.23E-01
22508268	C04717	CCCCC(CCCCCC=CC=CC(=O)O)OO	Hydroperoxyoctadecadienoic acid	1.86E+05	4.12E-03	1.66E-01	2.92E-06
5312869	C22001	CCCCCCCCC(C(=O)O)O	Hydroxymyristic acid	1.00E+00	5.00E-02	1.00E+00	5.00E-02
5810	C01157	C1C(CNC1C(=O)O)O	Hydroxyproline	1.31E+05	5.51E-05	3.50E-03	5.55E-24
144	C01017	C1=CC2=C(C=C1O)C(=CN2)CC(C(=O)O)N	Hydroxytryptophan	4.01E+05	1.86E-10	8.07E-02	3.79E-13
440406	C04611	C1C(C(C(C(O1)OC2C(C(C(C2O)O)OC(=O)CC3=CN4=CC=CC=C43)O)O)O)O	Indolyl acetyl myoinositol arabinoside	1.00E+00	5.00E-02	1.00E+02	1.50E-02
6306	C00407	CCC(C)C(C(=O)O)N	Isoleucine	8.94E-01	6.57E-02	5.25E-01	2.29E-03
5280804	C05623	C1=CC(=C(C=C1C2=C(C(=O)C3=C(C=C(C3O2)O)O)OC4C(C(C(C4)CO)O)O)O)O	Isoquercitin	1.00E+00	5.00E-02	1.00E+00	5.00E-02
5280863	C05903	C1=CC(=CC=C1C2=C(C(=O)C3=C(C=C(C3O2)O)O)O)O	Kaempferol	7.63E-01	2.42E-02	1.00E+02	6.53E-06
583024	C12634	OC[C@H]1O[C@@H](O[C@H]2[C@H](Oc3c(oc4cc(O)cc(O)c4c3=O)-c3ccc(O)cc3)O[C@H](CO)[C@@H](O)[C@H]2O)[C@H](O)[C@@H](O)[C@@H]1O	Kaempferol diglucosyl-glucoside	8.79E-01	3.83E-01	7.48E-01	3.34E-02
5480982	C12249	C1=CC(=CC=C1C2=C(C(=O)C3=C(C=C(C3O2)OC4C(C(C(C4)CO)O)O)O)O)O	Kaempferol glucoside	1.00E+00	5.00E-02	1.00E+02	1.42E-04
104152	C00047	CC(=O)O.C(CCN)CC(C(=O)O)N	Lysine acetate	2.63E+05	2.58E-02	8.71E-02	3.91E-04
525	C00149	C(C(C(=O)O)O)C(=O)O	Malic acid	8.72E-01	3.35E-01	2.55E+00	4.45E-10
442428	C09789	CC1C(C(C(C(O1)OC2C(C(C(OC2OC3=CC(=C4C(=O)CC(OC4=C3)C5=CC=C(C=C5)O)O)CO)O)O)O)O	Naringin	4.23E-01	1.26E-01	1.84E+00	1.27E-01
445638	C08362	CCCCC=CCCCCCCC(=O)O	Palmitoleic acid	4.14E+05	2.65E-02	1.89E-01	2.78E-02
6140	C02057	C1=CC=C(C=C1)CC(C(=O)O)N	Phenylalanine	9.55E-01	8.85E-01	1.00E-02	6.97E-10
91493	C04442	C(C(C(C(C(=O)O)O)O)O)OP(=O)(O)O	Phosphogluconate	4.22E-01	2.19E-03	6.49E+00	1.12E-11
115244	C10172	C[N+](CCCC1C(=O)[O-])C	Proline betaine	1.00E+00	5.00E-02	1.00E+02	1.53E-02
5280343	C00389	C1=CC(=C(C=C1C2=C(C(=O)C3=C(C=C(C3O2)O)O)O)O)O	Quercetin	9.19E-01	2.38E-01	1.11E+00	1.75E-01
5280459	C01750	CC1C(C(C(C(O1)OC2=C(OC3=CC(=CC(=C3C2=O)O)O)C4=CC(=C(C=C4)O)O)O)O)O	Quercitrin	1.82E+05	4.15E-06	1.00E+02	6.03E-03
6508	C00296	C1C(C(C(C1C(=O)O)O)O)O	Quinic acid	1.12E+05	6.33E-01	1.29E+00	2.24E-01
5280805	C05625	CC1C(C(C(C(O1)OCC2C(C(C(C2OC3=C(OC4=CC(=CC(=C4C3=O)O)O)C5=CC(=C(C=C5)O)O)O)O)O)O)O	Rutin	2.70E+05	3.09E-01	2.25E+00	1.30E-01

338	C00805	C1=CC=C(C(=C1)C(=O)O)O	Salicylic acid	3.43E+05	2.92E-06	5.48E-01	4.53E-04
5280665	C01175	COC1=CC(=CC(=C1O)OC)C=CC(=O)OC2C(C(C(OC2OC(=O)C=CC3=CC(=C(C(=C3)OC)O)OC)CO)O)O	Sinapoylglycoside	5.74E-01	3.08E-06	8.42E-01	1.14E-01
11953815	C02887	COC1=CC(=CC(=C1O)OC)C=CC(=O)OC(CC(=O)O)C(=O)O	Sinapoylmalate	7.75E-01	1.82E-01	1.14E-01	7.33E-06
1103	C00750	C(CCNCCCN)CNCCCN	Spermine monoaldehyde	1.00E+00	5.00E-02	1.00E+02	7.37E-03
65576	C10826	CC1CCC2(C(C3C(O2)CC4C3(CCC5C4CCC6C5(CCC(C6)O)C)C)C)NC1	Tomatidine	1.00E+00	5.00E-02	1.00E+02	6.28E-04
28523	C10827	CC1CCC2(C(C3C(O2)CC4C3(CCC5C4CCC6C5(CCC(C6)OC7C(C(C(C(O7)CO)OC8C(C(C(C(O8)CO)O)OC9C(C(C(CO9)O)O)O)OC2C(C(C(C(O2)C)O)O)O)O)C)C)C)NC1	Tomatine	9.10E-01	2.41E-01	8.35E-01	5.72E-03
14777879	C18069	C1=CC(=CC=C1C=CC(=O)NCCCCN(CCCNC(=O)C=CC2=CC=C(C=C2)O)C(=O)C=CC3=CC=C(C=C3)O)O	Tricoumaroylspermidine	1.09E+05	8.73E-01	1.00E-02	1.75E-03
6305	C00806	C1=CC=C2C(=C1)C(=CN2)CC(C(=O)O)N	Tryptophan	1.10E+05	3.02E-01	8.74E-01	1.71E-01
15376	C09251	CCC12CCCN3C1C4=C(CC3)C5=CC=CC=C5N4C(C2)(C(=O)OC)O	Vincamine	1.00E+00	5.00E-02	1.00E+00	5.00E-02
5280441	C01460	C1=CC(=CC=C1C2=CC(=O)C3=C(O2)C(=C(C=C3O)O)C4C(C(C(C(O4)C)O)O)O)O	Vitexin	8.76E-01	3.78E-02	8.61E-01	5.80E-03

Table S2: An overview of all metabolites detected and annotated from all different treatments (T1-T6) at all time -points _days 1, 3, 7 and 28).

Metabolite ID	Abbr.	Rt (min)	m/z	Diagnostic Fragment Ions	Adducts	Molecular Formula	Molecular Weight	Metabolite Class
Malic acid	MA	0.96	133.01	115	[M - H] ⁻	C ₄ H ₆ O ₅	134.09	Organic acid
Coumaroyl-glucaric acid	CouGA	3.51	355.07	257, 220,129		C ₁₅ H ₁₈ O ₈	326	HCA-sugar
Dehydrotomatine (I)	DHT (I)	6.3	1031.55	898, 868, 576	[M - H] ⁻	C ₅₀ H ₈₁ NO ₂₁	1032.5	Glycoalkaloid
Hydroxyproline	Hpro	4.72	149.10	84,59	[M-OH] ⁻	C ₅ H ₉ NO ₃	131.13	Amino acid
Salicylic acid	SA	6.86	137.02	93	[M - H] ⁻	C ₇ H ₆ O ₃	138.12	HCA
Glutamate	Glu	6.25	148.10	147, 128	[M + H] ⁺	C ₅ H ₉ O ₄	147.12	Amino acid

Alanyl-alanine	AIA	2.16	178.12	86, 91	[M + H] ⁺	C ₆ H ₁₂ N ₂ O ₃	160.17	Amino acid
Acetyl-leucine	AL	4.9	174.10	86	[M + H] ⁺	C ₈ H ₁₅ NO ₃	173.21	Amino acid
Ascorbic acid	AA	5.48	175.02	147, 87, 69	[M - H] ⁻	C ₆ H ₈ O ₆	176.12	Organic acid
Carbamoyl-aspartate	CLA	5	177.05	134	[M + H] ⁺	C ₅ H ₈ N ₂ O ₅	176.13	Amino acid
Glycyl-leucine	GL	5.4	189.12	86, 55, 30	[M + H] ⁺	C ₈ H ₁₆ N ₂ O ₃	188.22	Amino acid
Quinic acid	QA	4.4	191.05	175, 156, 146	[M - H] ⁻	C ₇ H ₁₂ O ₆	192.17	Organic acid
Carbamyl-methionine	CAM	3.74	191.05	150	[M + H] ⁺	C ₆ H ₁₂ N ₂ O ₃ S	192.24	Amino acid
Ferulic acid	FA	6.96	193.05	178, 149, 134	[M - H] ⁻	C ₁₀ H ₁₀ O ₄	194.18	HCA
Glutamine butyl ester	GTBE	6.16	220.17	156, 128	[M - H] ⁻	C ₉ H ₁₈ N ₂ O ₃	202.25	Amino acid
Ganic Lysine acetate	LysA	4.71	207.13		[M + H] ⁺	C ₈ H ₁₈ N ₂ O ₄	206.24	Amino acid
Hydroxytryptophan	Htrp	1.56	219.08	202, 160, 132	[M - H] ⁻	C ₁₁ H ₁₂ N ₂ O ₃	220.22	Amino acid
Chorismic acid	CHA	5.37	225.04	189, 171	[M - H] ⁻	C ₁₀ H ₁₀ O ₆	226.18	Organic acid
Hydroxymyristic acid	HmyrA	12.14	265.18	227	[M-OH] ⁻	C ₁₄ H ₂₈ O ₃	244.37	Organic acid
Acetyl-tryptophan	Atrp	5.75	245.09	216, 128, 98	[M - H] ⁻	C ₁₃ H ₁₄ N ₂ O ₃	246.26	Amino acid
Glutamyl-cystine	BGGC	8.45	499.12	128, 120, 82	[M-H] ⁻	C ₈ H ₁₄ N ₂ O ₅ S	250.3	Amino acid
Hexadecadienoic acid	HDDA	8.74	275.20		[M + Na] ⁺	C ₁₆ H ₂₈ O ₂	252.39	Fatty acid
Palmitoleic acid	PA	13.54	255.20	237, 219, 171	[M + H] ⁺	C ₁₆ H ₃₀ O ₂	254.41	Fatty acid
Phosphogluconate	Pglu	1.04	275.02	256, 176, 96	[M - H] ⁻	C ₆ H ₁₃ O ₁₀ P	276.14	Sugar
Quercetin	Que	5.82	301.05	284, 255, 227	[M - H] ⁻	C ₂₁ H ₂₀ O ₁₁	302.24	Flavonoid

Hydroperoxyoctadecadienoic acid	HPDA	12.9	311.22	206	[M - H] ⁻	C ₁₈ H ₃₂ O ₄	312.4	Fatty acid
Coumaroyl-quinic acid (I)	CouQA (I)	4.81	337.09	337, 163	[M - H] ⁻	C ₁₆ H ₁₈ O ₈	338.31	HCA
Coumaroyl-quinic acid (II)	CouQA (II)	4.59	337.09	337, 163, 145	[M - H] ⁻	C ₁₆ H ₁₈ O ₈	338.32	HCA
Sinapoyl-malate	SinM	2.75	385.08	223, 164, 149	[M - H] ⁻	C ₁₅ H ₁₆ O ₉	340.28	HCA-sugar
Caffeoyl-glycoside	Cgly	2.99	341.09	179, 135	[M - H] ⁻	C ₁₅ H ₁₈ O ₉	342.3	HCA-sugar
Feruloyl-quinic acid	FQA	4.93	367.10	193, 191	[M - H] ⁻	C ₁₇ H ₂₀ O ₉	368.3	HCA
Tomatidine	Tomd	7.37	416.35	398, 255	[M + H] ⁺	C ₂₇ H ₄₅ NO ₂	415.7	Glycoalkaloid
Kaempferol glucoside	Kglu	6.38	447.09	284, 255, 227	[M - H] ⁻	C ₂₁ H ₂₀ O ₁₁	448.4	Flavonoid-sugar
Quercitrin	Que	5.54	449.11	471, 449, 303	[M + H] ⁺	C ₂₁ H ₂₀ O ₁₁	448.4	Flavonoid
Indolyl-acetyl-myo-inositol arabinoside	IMIA	1.91	538.15		[M + HCOONa] ⁺	C ₂₁ H ₂₇ NO ₁₁	469.4	Sugar
Tri-coumaroyl-spermidine	TCS	8.29	584.27		[M + H] ⁺	C ₃₄ H ₃₇ N ₃ O ₆	583.7	Polyamine
Rutin	Rut	5.59	609.04	300.028, 271.025, 255.030, 151.002	[M - H] ⁻	C ₂₇ H ₃₀ O ₁₆	610.5	Flavonoid
Isoleucine	Ile	1.42	132.10	86	[M + H] ⁺	C ₆ H ₁₃ NO ₂	131.17	Amino acid
Caffeoyl-quinic acid	CQA (II)	3.8	353.09	191	[M - H] ⁻	C ₁₆ H ₁₈ O ₉	354.31	HCA
Feruloyl-glucose	Fer-Glu	4.28	355.10	193	[M - H] ⁻	C ₁₆ H ₂₀ O ₉	356.32	HCA-sugar
Isoquercitin	Ique	5.64	465.1	303	[M - H] ⁻	C ₂₁ H ₂₀ O ₁₂	464.1	Flavonoid
Phenylalanine	Phe	1.97	166.08	120 103	[M + H] ⁺	C ₉ H ₁₁ NO ₂	165.19	Amino acids

Caffeoyl-quinic acid (II)	CQA (III)	4.4	353.08	191 173 135	[M - H] ⁻	C ₁₆ H ₁₈ O ₉	354.31	HCA
Sinapoyl-glycoside	Sin-Gly	4.27	385.11	223 205 179	[M - H] ⁻	C ₁₇ H ₂₂ O ₁₀	386.3	HCA-sugar
Caffeoyl-quinic acid (IV)	CQA (IV)	4.57	353.05	191 179 173 135	[M - H] ⁻	C ₁₆ H ₁₈ O ₉	354.31	HCA
Caffeoyl-quinic acid (I)	CQA (I)	2.72	353.86	191 179 173 135	[M - H] ⁻	C ₁₆ H ₁₈ O ₉	354.32	HCA
Caffeoyl-glucaric acid (I)	CGA (I)	1.98	371.06	209 173 164 129	[M - H] ⁻	C ₁₅ H ₁₆ O ₁₁	354.33	HCA-sugar
Feruloyl-galactarate (I)	Fer-gal (I)	3.08	385.07	223 191 193 189	[M - H] ⁻	C ₁₆ H ₁₈ O ₁₁	356.534	HCA-sugar
Feruloyl-galactarate (II)	Fer-gal (II)	3.95	385.09	223 191 193 189	[M - H] ⁻	C ₁₆ H ₁₈ O ₁₁	356.535	HCA-sugar
Vitexin	Vit	5.71	431.09	341 311 283 269	[M - H] ⁻	C ₂₁ H ₂₀ O ₁₀	432.38	Flavonoid
Tryptophan	Trp	2.97	205.09	116, 142, 158	[M + H] ⁺	C ₁₁ H ₁₂ N ₂ O ₂	204.23	Amino acid
Citric acid	CA	1.22	191.017	173,129,111,85	[M - H] ⁻	C ₆ H ₈ O ₇	192.12	Organic acid
Caffeoyl-glucaric acid (III)	CGA (III)	1.52	371.06	209,173,129,85	[M - H] ⁻	C ₁₅ H ₁₆ O ₁₁	372.28	HCA-sugar
Caffeoyl-glucaric acid (II)	CGA (II)	1.75	371.06	209,173,143,129,85	[M - H] ⁻	C ₁₅ H ₁₆ O ₁₁	372.29	HCA-sugar
Kaempferol glucoside (I)	malonoyl-KMG (I)	4.24	533.09	285, 489	[M - H] ⁻	C ₂₄ H ₂₂ O ₁₄	534.4	Flavonoid-sugar
Kaempferol glucoside (II)	malonoyl-KMG (II)	4.07	533.09	285, 490	[M - H] ⁻	C ₂₄ H ₂₂ O ₁₄	534.4	Flavonoid-sugar
Argininosuccinate	Arg-succ	4.05	289.12		[M - H] ⁻	C ₁₀ H ₁₈ N ₄ O ₆	290.27	Amino acid
Naringin	Nar	5.77	579.17	271, 151	[M - H] ⁻	C ₂₇ H ₃₂ O ₁₄	580.54	Flavonoid

Kaempferol diglucoside	diglucosyl-	KDG	3.88	771.20		[M - H] ⁻	C ₃₃ H ₄₀ O ₂₁	773.19	Flavonoid-sugar
Kaempferol diglucosyl-glucoside	coumaroyl-	KCDG	6.52	917.24		[M - H] ⁻	C ₄₂ H ₄₆ O ₂₃	918.25	Flavonoid-sugar
Dehydrotomatine (II)		DHT (II)	7.22	1076.50		[M + HCOOH] ⁺	C ₅₀ H ₈₁ NO ₂₁	1032.5	Glycoalkaloid
Tomatine		Tom	7.39	1078.55	1034, 1016	[M + HCOOH] ⁺	C ₅₀ H ₈₃ NO ₂₁	1034.19	Glycoalkaloid
Proline betaine		PB	1.91	166.08	84	[M + Na] ⁺	C ₇ H ₁₃ NO ₂	143.18	Amino acid
Spermine monoaldehyde		SMA	1.93	328.14		[M + NaCl_HCOONa] ⁺	C ₁₀ H ₂₃ N ₃ O	201.26	Polyamine

Table S3: The most significantly altered pathways based on impact factor > 0.1, Holm adjusted *p*-value < 0.05 and FDR < 0.05. The indication letters correspond to the labelled pathways on the pathway impact plot (**Figure 3B**)

Pathways		Total	Hits	Holm value	<i>p</i> -	FDR	Impact	Metabolites (Abbreviations) ¹
Significant pathways based on impact factor								
E	Biosynthesis of secondary metabolites	5	4	1.44×10^{-3}		3.88×10^{-4}	1	CouA, C-CoA, Cou-CoA, F-CoA
F	Linoleic acid metabolism	4	1	1		1	1	Linoleate
D	Flavone and flavonol biosynthesis	10	5	2.51×10^{-3}		5.25×10^{-4}	0.85	Kae, Que, Qtrn, Kae-glu, Que-glu
C	Stilbenoid biosynthesis	8	5	6.2×10^{-4}		3.12×10^{-4}	0.735	Cou-CoA, Cou-SKA, CGA, C-CoA, F-CoA
B	Flavonoid biosynthesis	47	10	1.5×10^{-3}		3.88×10^{-4}	0.517	Cou-SKA, Cou-CoA, CGA, Kae, D-kae, C-CoA, Nar, F-CoA, Que
L	Phenylalanine metabolism	11	1	1		1	0.471	Phe

¹ CouA, Coumaric acid; C-CoA, Caffeoyl-CoA; Cou-CoA, Coumaroyl-CoA; F-CoA, Feruloyl-CoA; Kae, Kaempferol; Que, Quercetin; Qtrn, Quercetrin; glu, glucoside; SKA, shikimate; Nar, Naringin; Phe, Phenylalanine; Trp, Tryptophan; tyr, tyrosine; CHA, chorismic acid; AA, Ascorbic acid; GA, galactarate; Arg-Succ, arginino-succinate; Gln, Glutamine; Asp, Aspartate; MA, Malic acid; CA, Citric acid; FA, Ferulic acid; CQA, Caffeoyl-quinic acid; CGA, Chlorogenic acid; SinM, Sinapoy- malate; Sin-gly, Sinapoyl-glycoside.

A	Phenylpropanoid biosynthesis	46	12	1.7×10^{-5}	1.74×10^{-5}	0.389	FA, CQA, Cou-CoA, CGA, Phe, CouA, C-CoA, F-CoA, Sin-gly, TCS, SinM, F-CoA
I	Phe, tyr and trp biosynthesis	22	3	1	1.542×10^{-1}	0.228	CHA, Trp, Phe
K	Ascorbate and aldarate metabolism	18	2	1	1	0.216	AA, GA
H	Ala, asp and glu metabolism	22	4	1	1.542×10^{-1}	0.212	Arg-succ, Ala, Gln, Asp
M	Citrate cycle (TCA cycle)	20	2	1	1	0.149	MA, CA
Significant pathways based on FDR and P-value							
A	Phenylpropanoid biosynthesis	46	12	1.7E-05	1.74×10^{-5}	0.389	FA, CQA, Cou-CoA, CGA, Phe, CouA, C-CoA, F-CoA, Sin-gly, TCS, SinM, F-CoA
C	Stilbenoid biosynthesis	8	5	6.2×10^{-4}	3.12×10^{-4}	0.735	Cou-CoA, Cou-SKA, CGA, C-CoA, F-CoA
E	Biosynthesis of secondary metabolites -	5	4	1.44×10^{-3}	3.88×10^{-4}	1	CouA, C-CoA, Cou-CoA, F-CoA
B	Flavonoid biosynthesis	47	10	1.5×10^{-3}	3.88×10^{-4}	0.517	Cou-SKA, Cou-CoA, CGA, Kae, D-kae, C-CoA, Nar, F-CoA, Que
D	Flavone and flavonol biosynthesis	10	5	2.51×10^{-3}	5.25×10^{-4}	0.85	Kae, Que, Qtrn, Kae-glu, Que-glu
G	Aminoacyl-tRNA biosynthesis	46	6	2.567×10^{-1}	4.513×10^{-2}	0	Phe, Arg, Gln, Asp, Met, Ala, Ile, Leu, Thr, Trp