

Supplementary Table 1. List of *E. coli* metabolites identified in the literature.

Pathway	Class <sup>a</sup>	Metabolite	Abbreviation	KEGG ID <sup>b</sup>	Standard chemical	Analytical mode <sup>c</sup>	Solubility	Formula											Molecular weight	m/z <sup>d</sup>	Description
								C	H	N	O	P	S	Fe	Se	Co	Cl				
Acid fermentation	I	Acetaldehyde		C00084	+	Neutral	Hydrophilic	2	4	1								44.0262	—	Neutral and/or hydrophobic	
Pyruvic acid oxidation	I	Acetic acid		C00033	+	Anion	Hydrophilic	2	4	2								60.0211	59.0139	Included in the buffer solution	
Short fatty acid degradation	II	Acetoacetic acid		C00164	+	Anion	Hydrophilic	4	6	3								102.0317	101.0244	Unable to be detected in CE-MS	
Short fatty acid degradation	II	Acetoacetyl-CoA		C00332	+	Nucleotide	Hydrophilic	25	40	7	18	3	1					851.1363	850.1291		
Isoleucine biosynthesis	I	2-Aceto-2-hydroxybutyric acid	ZAZHBA	—	—	Anion	Hydrophilic	6	10	4								146.0579	145.0506		
Acetoin biosynthesis	I	Acetoin		C00466	+	Neutral	Hydrophilic	4	8	2								88.0524	—	Neutral and/or hydrophobic	
Valine biosynthesis	I	2-Acetylacetic acid	2-Ac	C06010	—	Anion	Hydrophilic	5	8	4								132.0423	131.0350		
Pyruvic acid oxidation	I	Acetyl-CoA	AcCoA	C00024	+	Nucleotide	Hydrophilic	23	38	7	17	3	1					809.1258	403.5556	Detected as divalent ion in MS	
Dihydrodrolic acid analog (in vitro)	VI	5-Acetyl-dihydrodrolic acid		C01136	—	Cation	Hydrophilic	10	19	1	2							249.0857	250.0930		
Peptidoglycan turnover	II	N-Acetyl-D-glucosamine	GlcNAc	C03000	—	Neutral	Hydrophilic	8	15	1	6							221.0899	—	Neutral and/or hydrophobic	
UDP-N-acetylglucosamine biosynthesis	I	N-Acetylglucosamine-1-phosphate	GlcNAc-P	C04256	+	Anion	Hydrophilic	8	16	1	9	1						301.0563	300.0490		
Glucosamine degradation	II	N-Acetyl-D-glucosamine-6-phosphate	NacGlcNP	C00357	+	Anion	Hydrophilic	8	16	1	9	1						301.0563	300.0490		
Arginine biosynthesis	I	N-Acetylglutamate semialdehyde	N-ACGlu-semialdehyde	C01250	—	Anion	Hydrophilic	7	11	1	4							173.0688	172.0615		
Arginine biosynthesis	I	N-Acetyl-L-glutamic acid	N-ACGlu	C00624	+	Cation	Hydrophilic	7	11	1	5							189.0637	190.0710		
Arginine biosynthesis	I	N-Acetylglutamylyphosphate	N-ACGlu-P	C04133	—	Anion	Hydrophilic	7	12	1	8	1						269.0301	268.0228		
Maltose assimilation	III	Acetylmaltose		C02130	—	Neutral	Hydrophilic	14	24	12								384.1268	—	Neutral and/or hydrophobic	
Acetylglucosamine dissimilation	II	N-Acetylmannosamine	ManNAc	C00645	+	Neutral	Hydrophilic	8	15	1	6							221.0899	—	Neutral and/or hydrophobic	
Acetylglucosamine dissimilation	II	N-Acetyl-D-mannosamine-6-phosphate	ManNAc6P	C04257	—	Anion	Hydrophilic	8	16	1	9	1						301.0563	300.0490		
Peptidoglycan biosynthesis	I	N-Acetylmuramoyl-L-alanyl-D-glutamyl-meso-2,6-diaminoheptane-D-alanyl-D-alaninediphosphoundecaprenol	MurNACAlaGluDAHeAlaAdePPUn	C05897	—	Nucleotide	Hydrophobic	87	143	7	23	2						1715.9711	1714.9638	Out of the MS range	
Acetylglucosamine dissimilation	II	N-Acetylneuraminic acid	NeuNAc	C00270	+	Anion	Hydrophilic	11	19	1	9							309.1060	308.0987		
Arginine biosynthesis	I	N-α-Acetylmethionine	N-ACOrn	C00437	+	Cation	Hydrophilic	7	14	2	3							174.1004	175.1077		
Pyruvic acid oxidation	I	Acetylphosphate	Ac-P	—	—	Anion	Hydrophilic	2	5	5	1							139.9875	138.9802		
Cysteine biosynthesis	I	O-Acetyl-L-serine	AcSer	C00979	+	Cation	Hydrophilic	5	9	1	4							147.0532	148.0604		
Polyamine acetylation	I	N <sup>1</sup> -Acetylspermidine	N1AcSpermidine	C00612	—	Cation	Hydrophilic	9	21	3	1							187.1685	188.1757		
Polyamine acetylation	I	N <sup>1</sup> -Acetylspermine	N1AcSpermine	C02567	+	Cation	Hydrophilic	12	28	4	1							244.2263	245.2336		
TCA cycle	I	cis-Aconitic acid		C00417	+	Anion	Hydrophilic	6	6	6								174.0164	173.0092		
Trans-Aconitic acid metabolism	III	trans-Aconitic acid		C02341	+	Anion	Hydrophilic	6	6	6								174.0164	173.0092		
Salvage of Ade, HypXan	I	Adenine		C00147	+	Cation	Hydrophilic	5	5									135.0545	136.0618		
Purine biosynthesis	I	Adenine-5-phosphate	AMP	C00020	+	Nucleotide	Hydrophilic	10	14	5	7	1						347.0631	346.0558		
Salvage of Ade, HypXan	I	Adenosine		C00212	+	Cation	Hydrophilic	10	13	5	4							267.0968	268.1040		
Sulfuric acid assimilation	I	Adenosine-3',5'-diphosphate	pAp	C00054	+	Nucleotide	Hydrophilic	10	15	5	10	2						427.0294	426.0221		
Purine biosynthesis	I	Adenosine-5'-diphosphate	ADP	C00008	+	Nucleotide	Hydrophilic	10	15	5	10	2						427.0294	426.0221		
ADP-ribose degradation (putative)	VI	Adenosinediphosphateribose	AdePPRI	C01882	+	Nucleotide	Hydrophilic	15	23	5	14	2						559.0717	558.0644		
Sulfuric acid assimilation	I	Adenosine-5'-phosphosulfate	APS	C00224	+	Nucleotide	Hydrophilic	10	14	5	10	1	1					427.0199	426.0126		
Purine biosynthesis	I	Adenosine-5'-triphosphate	ATP	C00002	+	Nucleotide	Hydrophilic	10	16	5	13	3						506.9958	505.9885		
Cobalamin biosynthesis	IV	Adenosylcobalamin-5'-phosphate	AdeC	—	—	Nucleotide	Hydrophobic	70	99	20	20	2			1			1658.5995	1657.5923	Out of the MS range	
Cobalamin biosynthesis	IV	Adenosylcobinamide		C06508	—	Cation	Hydrophobic	58	84	16	11				1			1237.5681	1238.5754	Out of the MS range	
Cobalamin biosynthesis	IV	Adenosylcobinamide phosphate	Adenosylcobinamide-P	—	—	Anion	Hydrophobic	58	83	16	14	1			1			1315.5188	1314.5115	Out of the MS range	
Cobalamin biosynthesis	IV	Adenosylcobinamide-GDP		C06510	—	Nucleotide	Hydrophobic	68	97	21	21	2			1			1662.5819	1661.5746	Out of the MS range	
Proto- and siroheme biosynthesis	I	5-Adenosylhomocysteine	SAHC	C00021	+	Cation	Hydrophilic	14	20	6	5	1						384.1216	385.1289		
Polyamine biosynthesis	I	5-Adenosylmethionine	dAdoMet	C01137	—	Cation	Hydrophilic	14	23	6	3	1						355.1552	355.1552	Including trinary sulfur	
SAM biosynthesis	I	5-Adenosyl-L-methionine	SAM	C00019	+	Cation	Hydrophilic	15	23	6	5	1						399.1451	399.1451	Including trinary sulfur	
Biotin biosynthesis	I	5-Adenosyl-4-methylthio-2-oxobutanoic acid	S4MT2OBA	C04425	—	Cation	Hydrophilic	15	20	5	6	1						398.1134	398.1134	Including trinary sulfur	
Purine biosynthesis	I	Adenylosuccinic acid	ASA	C03794	+	Nucleotide	Hydrophilic	13	16	5	11	1						449.0584	448.0511		
Glycogen biosynthesis	I	ADP-D-glucose	ADP-Glc	C00498	+	Nucleotide	Hydrophilic	16	25	5	15	2						589.0822	588.0750		
ADP-ribose degradation (putative)	VI	ADP-ribose		C00301	—	Nucleotide	Hydrophilic	15	23	5	14	2						559.0717	558.0644		
Polyamine biosynthesis	I	Agmatine		C00179	+	Cation	Hydrophilic	5	14	4								130.1218	131.1291		
Pantothenic acid biosynthesis	I	β-Alanine	β-Ala	C00099	+	Cation	Hydrophilic	3	7	1	2							89.0477	90.0550		
Peptidoglycan biosynthesis	I	D-Alanine	D-Ala	C00133	+	Cation	Hydrophilic	3	7	1	2							89.0477	90.0550		
Alanine biosynthesis	I	L-Alanine	Ala	C00041	+	Cation	Hydrophilic	3	7	1	2							89.0477	90.0550		
Peptidoglycan turnover	II	L-Alaninyl-γ-D-glutamyl-meso-diaminopimelyl-D-alanine	AlaGluDAPAla	—	—	Cation	Hydrophilic	16	27	5	9							433.1809	434.1882		
Peptidoglycan biosynthesis	I	D-Alanyl-D-alanine	AlaAla	C00993	+	Cation	Hydrophilic	6	12	2	3							160.0848	161.0921		
Peptidoglycan turnover	II	L-Alanyl-γ-D-glutamyl-L-glutamic acid	L-Ala-D-Glu	—	—	Cation	Hydrophilic	8	14	2	5							218.0903	219.0975	Multiple peaks were detected	
Peptidoglycan turnover	II	L-Alanyl-γ-D-glutamyl-diaminopimelic acid	L-Ala-D-Glu-Dap	—	—	Cation	Hydrophilic	13	19	4	4							309.1437	310.1510		
Peptidoglycan biosynthesis	I	L-Alanyl-D-glutamyl-meso-A2pm	AlaGluA2pm	—	—	Cation	Hydrophilic	15	26	4	8							390.1751	391.1823		
Allantoin degradation	III	Allantoic acid		C00499	+	Anion	Hydrophilic	4	8	4	4							176.0546	175.0473		
Allantoin degradation	III	Allantoin		C01551	+	Anion	Hydrophilic	4	6	4	3							158.0440	157.0367		
Lactose degradation	III	Allolactose		—	—	Neutral	Hydrophilic	12	22	11								342.1162	—	Neutral and/or hydrophobic	
Allose degradation	III	D-Allose		C01487	+	Neutral	Hydrophilic	6	12	6								180.0634	—	Neutral and/or hydrophobic	
Allose degradation	III	D-Allose-6-phosphate		C02962	—	Anion	Hydrophilic	6	13	9	1							260.0297	259.0224		
ItaE (in vitro)	VI	L-Allothreonine		C05519	+	Cation	Hydrophilic	4	9	1	3							119.0582	120.0655		
Allose degradation	III	D-Allulose-6-phosphate		—	—	Anion	Hydrophilic	6	13	9	1							260.0297	259.0224		
Galacturonic acid degradation	III	D-Altronic acid		C00817	—	Anion	Hydrophilic	6	12	7								196.0583	195.0510		
Taurine degradation	III	Aminoacetaldehyde		C06735	—	Cation	Hydrophilic	2	5	1	1							59.0371	60.0444		
Threonine degradation	III	Aminoacetone		C01888	—	Cation	Hydrophilic	3	7	1	1							73.0528	74.0600		
Tetrahydrofolic acid biosynthesis	I	p-Aminobenzoylserine	PABA	C00568	+	Cation	Hydrophilic	7	7	1	2							137.0477	138.0550		
Putrescine degradation	II	4-Aminobutyraldehyde	4ABA	C00555	—	Cation	Hydrophilic	4	9	1	1							87.0684	88.0757		
4-Aminobutyric acid degradation	III	4-Aminobutyric acid	4-AB	C00334	+	Cation	Hydrophilic	4	9	1	2							103.0633	104.0706		
Tetrahydrofolic acid biosynthesis	I	4-Amino-4-deoxychorismic acid	ADCA	C11355	—	Cation	Hydrophilic	10	11	5		</									

Menquinone biosynthesis	I	Demethylmenquinone-8	dMmEQ-8	—	—	Neutral	Hydrophobic	50	70	2								702.5376	—	Neutral and/or hydrophobic
Ubiquinone biosynthesis	I	3-Demethylubiquinone-8		C05815	—	Anion	Hydrophobic	48	72	4								712.5431	711.5358	Neutral and/or hydrophobic
NudB (in vitro)	VI	Deoxyadenine-5'-phosphate	dAMP	C00360	+	Cation	Hydrophilic	10	14	5	6	1						331.0682	332.0754	Neutral and/or hydrophobic
Purine biosynthesis	I	Deoxyadenine-5'-triphosphate	dATP	C00131	+	Nucleotide	Hydrophilic	10	16	5	12	3						491.0008	489.9936	
Salvage of Ade, HypXan	I	Deoxyadenosine	dAdenosine	C00559	+	Cation	Hydrophilic	10	13	5	3							251.1018	252.1091	
Purine biosynthesis	I	Deoxyadenosine-5'-diphosphate	dADP	C00206	+	Nucleotide	Hydrophilic	10	15	5	9	2						411.0345	410.0272	
Chorismic acid biosynthesis	I	3-Deoxy-D-arabinoheptulosonate-7-phosphate	3DAH7P	C04691	—	Anion	Hydrophilic	7	13	10	10	1						288.0246	287.0174	
Pyrimidine biosynthesis	I	Deoxycytidine-5'-diphosphate	dCDP	C00705	+	Nucleotide	Hydrophilic	9	15	3	10	2						387.0233	386.0160	
Salvage of pyrimidine	I	Deoxycytidine	dCyt	C00881	+	Cation	Hydrophilic	9	13	3	4							227.0926	228.0979	
NudB (in vitro)	VI	deoxycytidine-5'-phosphate	dCMP	C00239	+	Nucleotide	Hydrophilic	9	14	3	7	1						307.0569	306.0497	
Pyrimidine biosynthesis	I	Deoxycytidine-5'-triphosphate	dCTP	C00458	+	Nucleotide	Hydrophilic	9	18	3	13	3						469.0053	467.9980	
Salvage of Gua, Xan	I	Deoxyguanosine	dGuanosine	C00330	+	Cation	Hydrophilic	10	13	5	4							267.0968	268.1040	
NudB (in vitro)	VI	Deoxyguanosine-5'-phosphate	dGMP	C00362	+	Nucleotide	Hydrophilic	10	14	5	7	1						347.0631	346.0558	
Purine biosynthesis	I	Deoxyguanosine-5'-triphosphate	dGTP	C00286	+	Nucleotide	Hydrophilic	10	15	5	13	3						505.9879	504.9807	
Purine biosynthesis	I	Deoxyguanosone-5'-diphosphate	dGDP	C00361	+	Nucleotide	Hydrophilic	10	15	5	10	2						427.0294	426.0221	
Salvage of Ade, HypXan	I	Deoxyinosine	dInosine	C05512	+	Cation	Hydrophilic	10	12	4	4							252.0859	253.0931	
ITP, XTP dephosphorelation	IV	Deoxyinosine-5'-phosphate	dIMP	C06196	+	Nucleotide	Hydrophilic	10	13	4	7	1						332.0522	331.0449	
ITP, XTP dephosphorelation	IV	Deoxyinosine-5'-triphosphate	dITP	C01345	+	Nucleotide	Hydrophilic	10	15	4	13	3						491.9849	490.9776	
KDO biosynthesis	I	3-Deoxy-D-mannoctulosonate-8-phosphate	DManOP	C04478	—	Anion	Hydrophilic	8	15	11	1							318.0352	317.0279	
KDO biosynthesis	I	3-Deoxy-D-manno-octulosonic acid	DManOA	C01187	—	Anion	Hydrophilic	8	14	8								238.0689	237.0616	
Salvage of Gua, Xan	I	Deoxyribose-1-phosphate	dR1P	C00672	+	Anion	Hydrophilic	5	11	7	1							214.0242	213.0170	
Ribosephosphate degradation	II	Deoxyribose-5-phosphate	dR5P	C00673	+	Anion	Hydrophilic	5	11	7	1							214.0242	213.0170	
Pyrimidine biosynthesis	I	Deoxythymidine-5'-phosphate	dTMP	C00364	+	Nucleotide	Hydrophilic	10	15	2	8	1						322.0566	321.0493	
Pyrimidine biosynthesis	I	Deoxythymidine-5'-triphosphate	dTTP	C00459	+	Nucleotide	Hydrophilic	10	17	2	14	3						481.9893	480.9820	
Pyrimidine biosynthesis	I	Deoxythymidine-5'-diphosphate	dTDP	C00363	+	Nucleotide	Hydrophilic	10	16	2	11	2						402.0229	401.0157	
Salvage of pyrimidine	I	Deoxyuridine	dUrid	C00526	+	Cation	Hydrophilic	9	12	2	5							228.0746	229.0819	
Pyrimidine biosynthesis	I	Deoxyuridine-5'-diphosphate	dUDP	C01346	+	Nucleotide	Hydrophilic	9	14	2	11	2						388.0073	387.0000	
Pyrimidine biosynthesis	I	Deoxyuridine-5'-phosphate	dUMP	C00365	+	Nucleotide	Hydrophilic	9	13	2	8	1						308.0410	307.0337	
Pyrimidine biosynthesis	I	Deoxyuridine-5'-triphosphate	dUTP	C00460	+	Nucleotide	Hydrophilic	9	15	2	14	3						467.9736	466.9663	
1-Deoxy-D-xylulose assimilation	III	1-Deoxy-D-xylulose	dXylulose	C06257	—	Neutral	Hydrophilic	5	10	4								134.0579	—	Neutral and/or hydrophobic
Pyridoxal-5'-phosphate biosynthesis	I	1-Deoxy-D-xylulose-5-phosphate	1DX5P	C11437	—	Anion	Hydrophilic	5	11	7								214.0242	213.0170	
CoA biosynthesis	I	Dephospho-CoA	dePCoA	C00882	+	Nucleotide	Hydrophilic	21	35	7	13	2	1					687.1489	686.1416	
Biotin biosynthesis	I	Dethiobiotin		C01909	+	Cation	Hydrophilic	10	18	2	3							214.1317	215.1390	
Acetoin biosynthesis	I	Diacetyl		C00741	+	Neutral	Hydrophilic	4	6	2								86.0368	—	Neutral and/or hydrophobic
Chitobiose transport	III	Diacetylchitobiose-6-phosphate	Diacetylchitobiose6P	—	—	Anion	Hydrophilic	16	29	2	15	1						520.1306	519.1233	
Fravrin biosynthesis	I	2,5-Diamino-6-(ribosylamino)-4-(3H)-pyrimidinone-5-phosphate	2_5DA6RA4P5P	C01304	—	Anion	Hydrophilic	9	16	5	8	1						353.0737	352.0664	
Biotin biosynthesis	I	7,8-Diaminononanoic acid	7_8DANA	C01037	—	Cation	Hydrophilic	9	20	2	2							188.1525	189.1598	
Lysine biosynthesis	I	L,L-Diaminopimelic acid	DPA	C00666	+	Anion	Hydrophilic	7	14	2	4							190.9954	189.0881	
Lysine biosynthesis	I	meso-Diaminopimelic acid	meso-DPA	C00680	—	Anion	Hydrophilic	7	14	2	4							190.9954	189.0881	
YgeX	VI	2,3-Diaminopropionic acid		C06393	+	Cation	Hydrophilic	3	8	2	2							104.0586	105.0659	
Enterobactin biosynthesis	IV	2,3-Dihydro-2,3-dihydroxybenzoic acid		C04171	—	Anion	Hydrophilic	7	8	4								156.0423	155.0350	
Phenylacetic acid degradation	III	cis-Dihydrodiol derivative of phenylacetyl-CoA		—	—	Nucleotide	Hydrophilic	29	44	7	19	3	1					919.1626	918.1553	
Lysine biosynthesis	I	L,2,3-Dihydrodipicolinic acid	2_3-DPA	C03340	—	Anion	Hydrophilic	7	7	1	4							169.0375	168.0302	
Tetrahydrofolic acid biosynthesis	I	7,8-Dihydrofolic acid	DHFA	C00415	+	Cation	Hydrophilic	19	21	7	6							443.1553	444.1626	
Dihydrofolic acid analog (in vitro)	VI	Dihydrofolic acid	DHFA	C00579	—	Cation	Hydrophilic	8	17	1	1	2						207.0752	208.0824	
Lipic acid recycling	III	Dihydrofolic acid	DHLA	C02147	—	Anion	Hydrophilic	8	16	2	2							208.0592	207.0519	
Tetrahydrofolic acid biosynthesis	I	Dihydroneopterin-3'-triphosphate	DHMTTP	—	—	Nucleotide	Hydrophilic	9	16	5	13	3						494.9958	493.9885	
Tetrahydrofolic acid biosynthesis	I	7,8-Dihydroneopterin	DHN	C04874	+	Cation	Hydrophilic	9	13	5	4							255.0968	256.1040	
Tetrahydrofolic acid biosynthesis	I	Dihydroneopterinophosphate	DHNMP	C05925	—	Nucleotide	Hydrophilic	9	14	5	7	1						335.0631	334.0558	
Tetrahydrofolic acid biosynthesis	I	7,8-Dihydroneopterin-3'-triphosphate	DHNTP	C04895	—	Nucleotide	Hydrophilic	9	16	5	13	3						494.9958	493.9885	
Pyrimidine biosynthesis	I	Dihydroorotic acid		C00337	+	Anion	Hydrophilic	5	6	2	4							158.0328	157.0255	
Dihydropterin regeneration (in vitro)	VI	6,7-Dihydropteridine		C05649	—	Cation	Hydrophilic	6	6	4								134.0592	135.0665	
Tetrahydrofolic acid biosynthesis	I	7,8-Dihydropteroic acid	DHPA	C00921	—	Cation	Hydrophilic	14	14	6	3							314.1127	315.1200	
YeiA, YeiT, YgfK (putative)	VI	Dihydrouracil		C00429	+	Neutral	Hydrophilic	4	6	2	2							114.0429	—	Neutral and/or hydrophobic
Glycerol degradation	III	Dihydroxyacetone		C00184	+	Neutral	Hydrophilic	3	6	3								90.0317	—	Neutral and/or hydrophobic
Glycolysis (Embden-Meyerhof-Parnas)	I	Dihydroxyacetonephosphate	DHAP	C00111	+	Anion	Hydrophilic	3	7	6	1							169.9980	168.9908	
Enterobactin biosynthesis	IV	2,3-Dihydroxybenzoic acid		C00196	+	Anion	Hydrophilic	7	6	4								154.0266	153.0193	
Enterobactin biosynthesis	IV	(2,3-Dihydroxybenzoyl)adenylic acid		C04030	—	Anion	Hydrophilic	17	18	5	10	1						483.0791	482.0719	
Enterobactin degradation	IV	2,3-Dihydroxybenzoylserine	2_3DHBSer	C04204	—	Anion	Hydrophilic	10	11	1	6							241.0586	240.0514	
Fravrin biosynthesis	I	3,4-Dihydroxy-2-butanone-4-phosphate	3_4D2B4P	C15556	—	Anion	Hydrophilic	4	9	6	1							184.0137	183.0064	
Valine biosynthesis	I	2,3-Dihydroxyisovaleric acid	2_3-DIV	C04039	—	Anion	Hydrophilic	5	10	4								134.0579	133.0506	
Isoleucine biosynthesis	I	2,3-Dihydroxy-3-methylvaleric acid	2_3DH3MVA	C04104	—	Anion	Hydrophilic	6	12	4								148.0736	147.0663	
Menquinone biosynthesis	I	1,4-Dihydroxy-2-naphthoic acid	1_4DHNapha	C03657	+	Anion	Hydrophilic	11	8	4								204.0423	203.0350	
HdhA (in vitro)	VI	3- $\alpha$ ,12- $\alpha$ -Dihydroxy-7-oxo-5- $\beta$ -cholanolic acid		C04643	—	Anion	Hydrophilic	24	38	5								406.2719	405.2646	
Phenylpropionic acid degradation	III	3-(2,3-Dihydroxyphenyl)propionic acid		C04044	—	Anion	Hydrophilic	9	10	4								182.0579	181.0506	
Ketogluconic acid metabolism	III	2,5-Diketeto-D-gluconic acid		C02780	—	Anion	Hydrophilic	6	8	7								192.0270	191.0197	
YiaK	VI	2,3-Diketeto-L-gulononic acid		C04575	—	Anion	Hydrophilic	6	8	7								192.0270	191.0197	
Anaerobic respiration	IV	Dimethyl sulfide		C00580	+	Neutral	Hydrophilic	2	6			1						62.0190	—	Neutral and/or hydrophobic
Isopeptidylphosphate biosynthesis	I	Dimethylallylpyrophosphate	DMAProp	C00235	+	Anion	Hydrophilic	5	12	7	2							246.0058	244.9986	
Cobalamin biosynthesis	IV	Dimethylbenzimidazole		C03114	+	Cation	Hydrophilic	9	10	2					</					

ppGpp degradation	V	Guanosine-3'-phosphate 5'-phosphate	pGp	—	+	Nucleotide	Hydrophilic	10	15	5	11	2					443.0243	442.0171	Catalytic enzyme is unidentified.
Purine biosynthesis	I	Guanosine-5'-triphosphate	GTP	C00044	+	Nucleotide	Hydrophilic	10	16	5	14	3					522.9907	521.9834	
Inorganic metabolite	I	H <sub>2</sub> O		C00001	—												18.0106		Solvent
Arginine biosynthesis	I	HCO <sub>3</sub> <sup>-</sup>		C00288	+	Anion	Hydrophilic	1	1	3							60.9926	59.9853	Volatile
Proto- and siroheme biosynthesis	I	Heme O		C15672	—	Anion	Hydrophobic	49	58	4	5		1				836.3660	835.3527	Neutral and/or hydrophobic
Histidine biosynthesis	I	L-Histidinol		C01929	—	Cation	Hydrophilic	6	9	3	1						139.0746	140.0818	Intermediate of reaction
Histidine biosynthesis	I	L-Histidine		C00135	+	Cation	Hydrophilic	6	9	3	2						155.0695	156.0768	
Histidine biosynthesis	I	L-Histidinol		C00860	+	Cation	Hydrophilic	6	11	3	1						141.0902	142.0975	
Histidine biosynthesis	I	L-Histidinolphosphate		C01100	—	Nucleotide	Hydrophilic	6	12	3	4	1					221.0565	220.0493	
Methionine biosynthesis	I	Homocysteine		C05330	—	Cation	Hydrophilic	4	9	1	2	1					135.0354	136.0427	
Homoserine biosynthesis	I	L-Homoserine		C00263	+	Cation	Hydrophilic	4	9	1	3						119.0582	120.0655	
Homoserine transport	III	Homoserine lactone		—	—	Cation	Hydrophilic	4	7	1	2						101.0477	102.0550	
Sulfuric acid assimilation	I	Hydrogen sulfide		C00283	—	Cation	Hydrophilic	2	2			1					33.9877	34.9950	Out of the MS range
Phenylacetic acid degradation	III	3-Hydroxyadipyl-CoA		C14145	—	Nucleotide	Hydrophilic	27	44	7	20	3	1				911.1575	910.1502	
Ubiquinone biosynthesis	I	<i>p</i> -Hydroxybenzoic acid	PHBA	C00156	+	Anion	Hydrophilic	7	6	3							138.0317	137.0244	
Thiamine biosynthesis	I	4-Hydroxybenzylalcohol	4Hben-ol	—	—	Neutral	Hydrophilic	7	8	2							124.0524	—	Neutral and/or hydrophobic
Oxidation of nucleotides by reactive oxygen	III	2-Hydroxydeoxyadenosine-5'-triphosphate		—	—	Nucleotide	Hydrophilic	10	16	5	13	3					506.9958	505.9885	
Oxidation of nucleotides by reactive oxygen	III	8-Hydroxydeoxyguanosine-5'-triphosphate		—	—	Nucleotide	Hydrophilic	10	16	5	14	3					522.9907	521.9834	
2-Oxoglutaric acid reduction (in vitro)	VI	( <i>R</i> )-2-Hydroxyglutaric acid		C01087	—	Anion	Hydrophilic	5	8	5							148.0372	147.0299	
Propionic acid anabolism	III	( <i>S</i> )-2-Hydroxyglutaric acid		C02630	—	Anion	Hydrophilic	5	8	5							148.0372	147.0299	
L-4-Hydroxy-2-keto-glutaric acid degradation	III	L-4-Hydroxy-2-keto-glutaric acid		C01127	—	Anion	Hydrophilic	5	6	6							162.0164	161.0092	
Phenylpropionic acid degradation	III	2-Hydroxy-6-ketono-2,4-diene-1,9-dicarboxylic acid		C04479	—	Anion	Hydrophilic	9	10	6							214.0477	213.0405	
Phenylpropionic acid degradation	III	4-Hydroxy-2-ketovaleric acid		C03589	—	Anion	Hydrophilic	5	8	4							132.0423	131.0350	
Isopentenylidiphosphate biosynthesis	I	1-Hydroxy-2-methyl-2-( <i>E</i> )-butenyl-4-diphosphate	HMeBuPP	C11811	—	Anion	Hydrophilic	5	12	8	2						262.0007	260.9935	
Proto- and siroheme biosynthesis	I	Hydroxymethylbilane	HMB	C01024	—	Anion	Hydrophilic	40	46	4	17						854.2858	853.2785	
Tetrahydrofolic acid biosynthesis	I	6-Hydroxymethyldehydropterin	HMeDHP	C01300	—	Cation	Hydrophilic	7	9	5	2						196.0829	196.0829	
FrmA (in vitro)	VI	5-Hydroxymethylglutathione		C14180	—	Cation	Hydrophilic	11	19	3	7	1					337.0944	338.1017	
Thiamine biosynthesis	I	Hydroxymethylpyrimidine	HMePyr	C01279	—	Cation	Hydrophilic	6	9	3	1						139.0746	140.0818	
Thiamine biosynthesis	I	Hydroxymethylpyrimidinediphosphate	HMePyrP	C04956	—	Anion	Hydrophilic	6	10	3	4	1					219.0409	218.0336	
Phenylpropionic acid degradation	III	3-(2-Hydroxyphenyl)propionic acid	3HP	C01198	—	Anion	Hydrophilic	9	10	3							166.0630	165.0557	
Phenylpropionic acid degradation	III	3-(3-Hydroxyphenyl)propionic acid		C11457	—	Anion	Hydrophilic	9	10	3							166.0630	165.0557	
HyuA (in vitro)	VI	Hydroxyphenylthioantoin		—	—	Cation	Hydrophilic	9	8	2	3						192.0535	193.0608	
Tyrosine biosynthesis	I	<i>p</i> -Hydroxyphenylpyruvic acid	HPP	C01179	+	Anion	Hydrophilic	9	8	4							180.0423	179.0350	
Pyridoxal-5'-phosphate biosynthesis	I	3-Hydroxy-4-phospho-hydroxy- $\alpha$ -ketobutyric acid	3H4PHKBA	—	—	Anion	Hydrophilic	4	6	8	1						212.9800	211.9728	
Glycolic acid degradation	III	Hydroxypyruvic acid		C00168	+	Anion	Hydrophilic	3	4	4							104.0110	103.0037	
Salvage of Ade, HypXan	I	Hypoxanthine		C00262	+	Cation	Hydrophilic	5	4	4	1						136.0385	137.0458	
Ketogluconic acid metabolism	III	L-Idonic acid		C00770	—	Anion	Hydrophilic	6	12	7							196.0583	195.0510	
Histidine degradation	II	Imidazole lactic acid	Im-lactate	C05568	—	Cation	Hydrophilic	6	8	2	3						156.0535	157.0608	
Histidine biosynthesis	I	Imidazoleacetolphosphate	IAP	C01267	—	Nucleotide	Hydrophilic	6	9	2	5	1					220.0249	219.0176	
Histidine degradation	II	Imidazolepyruvic acid	Im-pyruvic acid	C03277	—	Cation	Hydrophilic	6	6	2	3						154.0372	155.0451	
NAD biosynthesis	I	Iminoaspartic acid		C05840	—	Cation	Hydrophilic	4	5	1	4						131.0219	132.0291	
Tryptophan biosynthesis	I	Indole		C00463	+	Cation	Hydrophilic	8	7	1							117.0578	118.0651	
Tryptophan biosynthesis	I	Indole-3-glycerolphosphate	IG-P	C03506	—	Nucleotide	Hydrophilic	11	14	1	6	1					287.0559	286.0486	
Salvage of Ade, HypXan	I	Inosine		C00294	+	Cation	Hydrophilic	10	12	4	5						268.0808	269.0880	
Purine biosynthesis	I	Inosine-5'-phosphate	IMP	C00130	+	Nucleotide	Hydrophilic	10	13	4	8	1					348.0471	347.0398	
ITP, XTP dephosphorelation	IV	Inosine-5'-triphosphate	ITP	C00081	+	Nucleotide	Hydrophilic	10	15	4	14	3					507.9798	506.9725	
Inositol utilization (SuhB)	VI	<i>myo</i> -Inositol		C00137	+	Neutral	Hydrophilic	6	12	6							180.0634	—	Neutral and/or hydrophobic
Phytic acid degradation	III	<i>myo</i> -Inositolhexakisphosphate		C01204	+	Nucleotide	Hydrophilic	6	18	24	6						659.8614	658.8541	
Phytic acid degradation	III	<i>D-myo</i> -Inositol-1,2,3,4,5-pentakisphosphate		C04579	—	Nucleotide	Hydrophilic	6	17	21	5						579.8951	578.8878	
Phytic acid degradation	III	<i>D-myo</i> -Inositol-1,2,4,5,6-pentakisphosphate		C04563	—	Nucleotide	Hydrophilic	6	17	21	5						579.8951	578.8878	
Inositol utilization (SuhB)	VI	1L- <i>myo</i> -Inositol-1-phosphate		C04006	—	Anion	Hydrophilic	6	13	9	1						260.0297	259.0224	
Inositol utilization (SuhB)	VI	1D- <i>myo</i> -Inositol-1-phosphate		C01177	—	Anion	Hydrophilic	6	13	9	1						260.0297	259.0224	
Phytic acid degradation	III	<i>D-myo</i> -Inositol-2,3,4,5-tetraphosphate		—	—	Nucleotide	Hydrophilic	6	16	18	4						499.9287	498.9214	
Phytic acid degradation	III	<i>D-myo</i> -Inositol-2,4,5-triphosphate		—	—	Nucleotide	Hydrophilic	6	15	15	3						419.9624	418.9551	
Menaquinone biosynthesis	I	Ischorismic acid		C00885	—	Anion	Hydrophilic	10	10	6							226.0477	225.0405	
TCA cycle	I	Isocitric acid		C00311	+	Nucleotide	Hydrophilic	6	8	7							192.0270	191.0197	
Isoleucine biosynthesis	I	L-Isoleucine	Ile	C00407	+	Cation	Hydrophilic	6	13	1	2						131.0946	132.1019	
Isopentenylidiphosphate biosynthesis	I	$\Delta^3$ -Isopentenylidiphosphate	IPPP	C00129	—	Anion	Hydrophilic	5	12	7	2						246.0058	244.9986	
Leucine biosynthesis	I	2-Isopropylmalic acid	2IPMA	C02504	+	Anion	Hydrophilic	7	12	5							176.0685	175.0612	
Leucine biosynthesis	I	3-Isopropylmalic acid	3IPMA	C04411	—	Anion	Hydrophilic	7	12	5							176.0685	175.0612	
Leucine biosynthesis	I	2-Isopropyl-3-oxosuccinic acid	2IPJOSA	—	—	Anion	Hydrophilic	7	10	5							174.0528	173.0455	
AidA (in vitro)	VI	Isovaleryl-CoA		C02939	—	Nucleotide	Hydrophilic	26	44	7	17	3	1				851.1727	850.1655	
LipidA biosynthesis	I	KDO2-(lauroyl)-lipid IVA	KDO2-Lau-lipid IVA	C06251	—	Nucleotide	Hydrophobic	96	176	2	38	2					2027.1376	2026.1304	Out of the MS range
LipidA biosynthesis	I	KDO2-lipid A		C06026	—	Nucleotide	Hydrophobic	110	202	2	39	2					2237.3360	2236.3287	Out of the MS range
LipidA biosynthesis	I	KDO2-lipid A, cold adapted	KDO2-lipid A (cold)	—	—	Nucleotide	Hydrophobic	114	208	2	39	2					2291.3830	2290.3757	Out of the MS range
KDO biosynthesis	I	KDO2-lipid IVA		C06025	—	Nucleotide	Hydrophobic	84	154	2	37	2					1844.9706	1843.9633	Out of the MS range
LipidA biosynthesis	I	KDO2-(palmitoleoyl)-lipid IVA	KDO2-Pal-lipid IVA	—	—	Nucleotide	Hydrophobic	100	182	2	38	2					2081.1846	2080.1773	Out of the MS range
KDO biosynthesis	I	(KDO)-lipid IVA		C06024	—	Nucleotide	Hydrophobic	84	154	2	37	2					1844.9706	1843.9633	Out of the MS range
Phenylacetic acid degradation	III	$\beta$ -Ketoaldipyl-CoA		C02232	—	Nucleotide	Hydrophilic	27	42	7	20	3	1				909.1478	908.1346	
Galactaric acid degradation	III	5-Keto-4-deoxy-D-glucaric acid		C00679	—	Anion	Hydrophilic	6	8	7							192.0270	191.0197	
Entner-Doudoroff pathway	I	2-Keto-3-deoxy-6-phosphogluconic acid	KDPGcA	C04442	—	Anion	Hydrophilic	6	11	9	1						258.0141	257.0068	
Ketogluconic acid metabolism	III	5-Ketogluconic acid		C01062	—	Anion	Hydrophilic	6	10	7							194.0427	193.0354	
Ascorbic acid degradation	III	3-Keto-L-gulonate-6-phosphate		C14899	—	Anion	Hydrophilic	6	11	10	1						274.0090	273.0017	
Ketogluconic acid metabolism	III	2-Keto-L-gulonate acid		C15673	—	Anion	Hydrophilic	6	10	7							194.0427	193.0354	
Ascorbic acid degradation	III	3-Keto-L-gulonic acid		C00618	—	Anion	Hydrophilic	6	10	7							194.0427	193.0354	
Leucine biosynthesis	I	2-Ketoisovaleric acid	2KICA	C00233	+	Anion	Hydrophilic	6	10	3							130.0630	129.0557	
Valine biosynthesis	I	2-Ketoisovaleric acid	2-KIV	C00141	+	Anion	Hydrophilic	5	8	3							116.0473	115.0401	
Isoleucine biosynthesis	I	2-Keto-3-methylvaleric acid	2K3MVA	C03465	+	Anion	Hydrophilic	6	10	3							130.0630	129.0557	
Methylglyoxal pathway	I	D-Lactaldehyde	Lactaldehyde	C00424	—	Neutral	Hydrophilic	3	6	2							74.0368	—	Neutral and/or hydrophobic
Methylglyoxal pathway	I	D-Lactic acid		C00256	+	Anion	Hydrophilic	3	6	3							90.0317	89.0244	
Lactic acid fermentation	I	L-Lactic acid	Lactic acid	C01432	—	Anion	Hydrophilic	3	6	3							90.0317	89.0244	
Lactose degradation	III	Lactose		C00243	+	Neutral	Hydrophilic	12	22	11							342.1162	—	Neutral and/or hydrophobic
Methylglyoxal pathway	I	5-Lactoylglutathione	SL-GSH	C03451	+	Cation	Hydrophilic	13	21	3	8	1					379.1049	380.1122	
Leucine biosynthesis	I	L-Leucine	Leu	C00123	+	Cation	Hydrophilic	6	13	1	2								

Allantoin degradation	III	Oxalureatic acid			C00802	-	Anion	Hydrophilic	3	4	2	4								132.0171	131.0098		
Oxalic acid degradation	III	Oxalyl-CoA			C00313	-	Nucleotide	Hydrophilic	23	36	7	19	3	1							839.1000	838.0927	
Isoleucine biosynthesis	I	2-Oxobutanoic acid	2-OBa		C00109	+	Anion	Hydrophilic	4	6	3										102.0317	101.0244	
TCA cycle	I	2-Oxoglutaric acid	2-OG		C00026	+	Anion	Hydrophilic	5	6	3										146.0215	145.0142	
Phenylpropionic acid degradation	III	2-Oxopent-4-enoic acid			C00596	-	Anion	Hydrophilic	5	6	3										114.0317	113.0244	
PldC (in vitro)	VI	Palmitic acid			C00249	+	Anion	Hydrophilic	16	32	2										256.2402	255.2330	
CoA biosynthesis	I	Pantetheine-4-phosphate	P4P		C01134	-	Nucleotide	Hydrophilic	11	23	2	7	1	1							358.0964	357.0891	
Pantothenic acid biosynthesis	I	L-Pantoic acid	Pantoic acid		C00522	-	Anion	Hydrophilic	6	12	4										148.0736	147.0663	
Pantothenic acid biosynthesis	I	Pantothenic acid			C00864	+	Anion	Hydrophilic	9	17	1	5									219.1107	218.1034	
3-Hydroxybutyryl-CoA synthetase (B-specific)	VI	Pantoyllactone			C01012	+	Neutral	Hydrophilic	6	10	3										130.0630	-	Neutral and/or hydrophobic
Phenylethylamine degradation	III	Phenylacetaldehyde			C00601	+	Neutral	Hydrophilic	8	8	1										120.0575	-	Neutral and/or hydrophobic
Phenylacetic acid degradation	III	Phenylacetic acid			C07086	-	Anion	Hydrophilic	8	8	2										136.0524	135.0452	
Phenylacetic acid degradation	III	Phenylacetyl-CoA			C00582	+	Nucleotide	Hydrophilic	29	42	7	17	3	1							885.1571	884.1498	
D-Amino acids degradation	III	D-Phenylalanine	D-Phe		C02265	-	Cation	Hydrophilic	9	11	1	2									165.0790	166.0863	
Phenylalanine biosynthesis	I	L-Phenylalanine	Phe		C00079	+	Cation	Hydrophilic	9	11	1	2									165.0790	166.0863	
Phenylethylamine degradation	III	Phenylethylamine			C05332	+	Cation	Hydrophilic	8	11	1										121.0891	122.0964	
HyuA (in vitro)	VI	Phenylhydantoin			-	-	Cation	Hydrophilic	9	8	2	2									176.0586	177.0659	
Phenylpropionic acid degradation	III	3-Phenylpropionic acid	PPA		C05629	+	Anion	Hydrophilic	9	10	2										150.0681	149.0608	
Phenylalanine biosynthesis	I	Phenylpyruvic acid			C00166	+	Anion	Hydrophilic	9	8	3										164.0473	163.0401	
Sulfuric acid assimilation	I	3'-Phosphoadenosine-5'-phosphosulfate	PAPS		C00053	-	Nucleotide	Hydrophilic	10	15	5	13	2	1							506.9862	505.9790	
Glycolysis (Embden-Meyerhof-Parnas)	I	Phosphoenolpyruvic acid	PEP		C00074	+	Anion	Hydrophilic	3	5	6	1									167.9824	166.9751	
Pentose phosphate pathway (oxidative)	I	6-Phospho-D-gluconic acid	6-PG		C00345	+	Anion	Hydrophilic	6	13	10	1									276.0246	275.0174	
6-Phospho-β-glucosidase (cryptic)	VI	6-Phospho-β-D-glucoside-(1,4)-D-glucose			-	-	Anion	Hydrophilic	12	23	14	1									422.0825	421.0753	
Glycolysis (Embden-Meyerhof-Parnas)	I	2-Phosphoglyceric acid	2-PG		C00631	+	Anion	Hydrophilic	3	7	7	1									185.9929	184.9857	
Glycolysis (Embden-Meyerhof-Parnas)	I	3-Phosphoglyceric acid	3-PG		C00597	+	Anion	Hydrophilic	3	7	7	1									185.9929	184.9857	
Gph (in vitro)	VI	2-Phosphoglyceric acid			C00988	-	Anion	Hydrophilic	2	5	6	1									155.9824	154.9751	
Threonine biosynthesis	I	O-Phospho-L-homoserine	P-HomoSer		C01102	-	Anion	Hydrophilic	4	10	1	6	1								199.0246	198.0173	
Serine biosynthesis	I	3-Phosphohydroxypyruvic acid	3PHPA		C03232	-	Anion	Hydrophilic	3	5	7	1									183.9773	182.9700	
Pyridoxal-5'-phosphate biosynthesis	I	Phosphohydroxythreonine	PHThr		-	-	Anion	Hydrophilic	4	9	1	7	1								214.0117	213.0044	
CoA biosynthesis	I	D-4-Phosphopantothenic acid	4PPA		C03492	-	Nucleotide	Hydrophilic	9	18	1	8	1								299.0770	298.0697	
CoA biosynthesis	I	4'-Phospho-N-pantothenoylcysteine	4PPC		C04352	-	Nucleotide	Hydrophilic	12	23	2	9	1								402.0862	401.0789	
Purine biosynthesis	I	5-Phosphoribosylamine	PRA		C03090	-	Nucleotide	Hydrophilic	5	12	1	7	1								229.0351	228.0279	
Histidine biosynthesis	I	Phosphoribosyl-AMP	PR-AMP		C02741	-	Nucleotide	Hydrophilic	15	23	5	14	2								559.0717	558.0644	
Tryptophan biosynthesis	I	N-(5-Phosphoribosyl)anthranilic acid	PRAnth		C04302	-	Nucleotide	Hydrophilic	12	16	1	9	1								349.0563	348.0490	
Histidine biosynthesis	I	Phosphoribosyl-ATP	PR-ATP		C02739	-	Nucleotide	Hydrophilic	15	25	5	20	4								719.0043	717.9971	
Purine biosynthesis	I	5-Phosphoribosyl-4-carboxy-5-aminoimidazole	CAIR		C04751	-	Nucleotide	Hydrophilic	9	14	3	9	1								339.0468	338.0395	
PRPP biosynthesis	I	5-Phosphoribosylidiphosphate	PRPP		C00119	+	Nucleotide	Hydrophilic	5	13	14	3									389.9518	388.9445	
Purine biosynthesis	I	Phosphoribosylformamidocarboxamide	FAICAR		-	-	Nucleotide	Hydrophilic	10	15	4	9	1								366.0577	365.0504	
Histidine biosynthesis	I	Phosphoribosylformimino-AICAR-phosphate	PRFAP		C04896	-	Nucleotide	Hydrophilic	15	25	5	15	2								577.0822	576.0750	
Purine biosynthesis	I	5-Phosphoribosyl-N-formylglycineamide	FGAR		C04376	-	Nucleotide	Hydrophilic	8	15	2	9	1								314.0515	313.0442	
Purine biosynthesis	I	5-Phosphoribosyl-N-formylglycineamide	FGAM		C04640	-	Nucleotide	Hydrophilic	8	16	3	8	1								313.0675	312.0602	
Purine biosynthesis	I	5-Phosphoribosylglycineamide	GAR		C03838	-	Nucleotide	Hydrophilic	7	15	2	8	1								286.0566	285.0493	
Purine biosynthesis	I	5-Phosphoribosyl-4-(N-succinocarboxamide)-5-aminoimidazole	SAICAR		C04823	-	Nucleotide	Hydrophilic	13	19	4	12	1								454.0737	453.0664	
Histidine biosynthesis	I	Phosphoribosylformimino-AICAR-phosphate	PRuFAP		C04916	-	Nucleotide	Hydrophilic	15	25	5	15	2								577.0822	576.0750	
Serine biosynthesis	I	3-Phosphoserine	3PSer		C01005	+	Anion	Hydrophilic	3	8	1	6	1								185.0089	184.0017	
Biotin biosynthesis	I	Pimelic acid			C02656	+	Anion	Hydrophilic	7	12	4										160.0736	159.0663	
Biotin biosynthesis	I	Pimeloyl-CoA			C01063	-	Nucleotide	Hydrophilic	28	46	7	19	3	1							909.1782	908.1709	
Proto- and siroheme biosynthesis	I	Porphobilinogen			C00931	+	Cation	Hydrophilic	10	14	2	4									226.0954	227.1026	
Proto- and siroheme biosynthesis	I	Precorrin-1			C15527	-	Anion	Hydrophilic	41	46	4	16									850.2929	849.2836	
Proto- and siroheme biosynthesis	I	Precorrin-2			C02463	-	Anion	Hydrophilic	42	48	4	16									864.3065	863.2993	
Molybdopterin biosynthesis	I	Precursor-Z	Precursor-Z		-	-	Cation	Hydrophilic	10	12	5	7	1								345.0474	346.0547	
Prephenic acid biosynthesis	I	Prephenic acid			C00254	+	Anion	Hydrophilic	10	10	6										226.0477	225.0405	
Proline biosynthesis	I	L-Proline	Pro		C00148	+	Cation	Hydrophilic	5	9	1	2									115.0633	116.0706	
Fucose degradation	III	Propane-1,2-diol			C00583	+	Neutral	Hydrophilic	3	8	2										76.0524	-	Neutral and/or hydrophobic
Threonine degradation	II	Propionic acid			C00163	+	Anion	Hydrophilic	3	6	2										74.0368	73.0295	
Threonine degradation	II	Propionyl-CoA			C00100	+	Nucleotide	Hydrophilic	24	40	7	17	3	1							823.1414	822.1342	
Threonine degradation	II	Propionylphosphate	Propionyl-P		C02876	-	Anion	Hydrophilic	3	7	5	1									154.0031	152.9958	
Proto- and siroheme biosynthesis	I	Protoheme IX			C00032	-	Anion	Hydrophilic	34	32	4	4									614.1616	613.1544	Detected as divalent ion in MS
Proto- and siroheme biosynthesis	I	Protoporphyrin IX	Por IX		C02191	+	Anion	Hydrophilic	34	34	4	4									562.2580	561.2507	
Proto- and siroheme biosynthesis	I	Protoporphyrinogen IX			C01079	-	Anion	Hydrophilic	34	40	4	4									564.2737	563.2664	
Pseudouridine 5'-phosphate biosynthesis (rRNA)	I	Pseudouridine-5'-phosphate	Pseudo5P		C01168	-	Nucleotide	Hydrophilic	9	13	2	9	1								324.0359	323.0286	Modified tRNA
Polyamine biosynthesis	I	Putrescine			C00134	+	Cation	Hydrophilic	4	12	2										88.1000	89.1073	
Pyrazinamide degradation	III	Pyrazinamide			C01956	+	Cation	Hydrophilic	5	5	3	1									123.0433	124.0505	
Pyrazinamide degradation	III	Pyrazinic acid			-	-	Cation	Hydrophilic	5	4	2	2									124.0273	125.0346	
Salvage of pyridoxal-5'-phosphate	I	Pyridoxal			C00250	+	Cation	Hydrophilic	8	9	1	3									167.0582	168.0655	
Pyridoxal-5'-phosphate biosynthesis	I	Pyridoxal-5'-phosphate	Pyr5P		C00018	+	Anion	Hydrophilic	8	10	1	6	1								247.0246	246.0173	
Salvage of pyridoxal-6'-phosphate	I	Pyridoxamine			C00534	+	Cation	Hydrophilic	8	12	2	2									168.0899	169.0972	
Salvage of pyridoxal-7'-phosphate	I	Pyridoxamine-5'-phosphate	PX5P		C00647	+	Anion	Hydrophilic	8	13	2	5	1								248.0562	247.0489	
Salvage of pyridoxal-8'-phosphate	I	Pyridoxine			C00314	+	Cation	Hydrophilic	8	11	1	3									169.0739	170.0812	
Pyridoxal-5'-phosphate biosynthesis	I	Pyridoxine-5'-phosphate	Pyn5P		C00627	-	Anion	Hydrophilic	8	12	1	6	1								249.0402	248.0330	
Inorganic metabolite	I	Pyrophosphate	PPi		C00013	+	Anion	Hydrophilic	4	4	2	2									177.9432	176.9360	
Proline biosynthesis	I	L-Δ <sup>1</sup> -Pyrroline-5-carboxylic acid	Pyrroline-5-carboxylate		C03912	+	Anion	Hydrophilic	5	7	1	2									113.0472	112.0404	
Quinones (pathway unknown)	V	Pyroloquinolinequinone	PQQ		C00113	+	Anion	Hydrophilic	14	6	2	8									330.0124	329.0051	
Glycolysis (Embden-Meyerhof-Parnas)	I	Pyruvic acid			C00022	+	Anion	Hydrophilic	3	4	3										88.0160	87.0088	
Queuine biosynthesis (tRNA)	I	Queuine			-	-	Cation	Hydrophilic	12	15	5	3									277.1175	278.1248	Modified tRNA
NAD biosynthesis	I	Quinolnic acid			C03722	+	Anion	Hydrophilic	7	5	1	4									167.0219	166.0146	
Rhamnose degradation	III	L-Rhamnose</																					

Quinones (pathway unknown)	V	Ubiquinone-2	CoQ2	--	--	Neutral	Hydrophobic	24	34	4								386.2457	--	Neutral and/or hydrophobic	
Quinones (pathway unknown)	V	Ubiquinone-3	CoQ3	--	--	Neutral	Hydrophobic	29	42	4									454.3083	--	Neutral and/or hydrophobic
Quinones (pathway unknown)	V	Ubiquinone-4	CoQ4	--	--	Neutral	Hydrophobic	34	50	4									522.3709	--	Neutral and/or hydrophobic
Quinones (pathway unknown)	V	Ubiquinone-5	CoQ5	--	--	Neutral	Hydrophobic	39	58	4									590.4335	--	Neutral and/or hydrophobic
Quinones (pathway unknown)	V	Ubiquinone-6		--	--	Neutral	Hydrophobic	39	58	4									590.4335	--	Neutral and/or hydrophobic
Quinones (pathway unknown)	V	Ubiquinone-6	CoQ6	--	--	Neutral	Hydrophobic	44	66	4									658.4961	--	Neutral and/or hydrophobic
Quinones (pathway unknown)	V	Ubiquinone-7	CoQ7	--	--	Neutral	Hydrophobic	49	74	4									726.5587	--	Neutral and/or hydrophobic
Ubiquinone biosynthesis	I	Ubiquinone-8	CoQ8	--	--	Neutral	Hydrophobic	49	74	4									726.5587	--	Neutral and/or hydrophobic
Quinones (pathway unknown)	V	Ubiquinone-9	CoQ9	C01967	+	Neutral	Hydrophobic	59	90	4									862.6839	--	Neutral and/or hydrophobic
Common antigen biosynthesis	I	UDP-N-acetyl-D-mannosamine	UDP-ManNAc	C01170	--	Nucleotide	Hydrophilic	17	27	3	17	2							607.0816	606.0743	
Common antigen biosynthesis	I	UDP-N-acetyl-D-mannosaminouronic acid	UDP-ManNAcUA	C06240	--	Nucleotide	Hydrophilic	17	25	3	18	2							621.0608	620.0536	
UDP-N-acetylglucosamine biosynthesis	I	UDP-N-acetyl-D-glucosamine	UDP-GlcNAc	C00043	+	Nucleotide	Hydrophilic	17	27	3	17	2							607.0816	606.0743	
Peptidoglycan biosynthesis	I	UDP-N-acetylmuramic acid	UDP-MurNAcA	C01050	--	Nucleotide	Hydrophilic	20	31	3	19	2							679.1027	678.0954	
Peptidoglycan biosynthesis	I	UDP-N-acetylmuramoyl-L-alanine	UDP-MurNAcAla	C01212	--	Nucleotide	Hydrophilic	23	36	4	20	2							750.1398	749.1325	
Peptidoglycan biosynthesis	I	UDP-N-acetylmuramoyl-L-alanyl-D-glutamic acid	UDP-GlcNAcMurAlaGlu	C00692	--	Nucleotide	Hydrophilic	28	43	5	23	2							879.1824	878.1751	
UshA (in vitro)	VI	UDP-N-acetylmuramoyl-L-alanyl-D-glutamyl-L-lysyl-D-alanyl-D-alanine	C04846	--	--	Nucleotide	Hydrophilic	40	65	9	26	2							1149.3516	1148.3443	Out of the MS range
Peptidoglycan biosynthesis	I	UDP-N-acetylmuramoyl-L-alanyl-D-glutamyl-meso-2,6-diaminoheptanedioic acid	UDP-GlcNAcMurAlaGluDAHeA	--	--	Nucleotide	Hydrophilic	35	54	7	26	2							1050.2594	1049.2521	Out of the MS range
Peptidoglycan turnover	II	UDP-N-acetylmuramoyl-L-alanyl-D-glutamyl-meso-2,6-diaminoheptanedioate-D-alanine	UDP-MurNAcAlaGluDAHeAAla	--	--	Nucleotide	Hydrophilic	38	60	8	27	2							1122.3043	1121.2970	Out of the MS range
Peptidoglycan biosynthesis	I	UDP-N-acetylmuramoyl-L-alanyl-D-glutamyl-meso-2,6-diaminoheptanedioate-D-alanyl-D-alanine	UDP-MurNAcAlaGluDAHeAAlaAla	C04882	--	Nucleotide	Hydrophilic	41	65	9	28	2							1193.3414	1192.3342	Out of the MS range
Modification of lipid A	I	UDP-4-amino-4-deoxy-L-arabinose	UDP-Ara4N	C16153	--	Nucleotide	Hydrophilic	14	22	3	15	2							534.0526	533.0453	
KDO biosynthesis	I	UDP-2,3-bis(3-hydroxymyristoyl)glucosamine	UDP-BHMyrGlc	C04652	--	Nucleotide	Hydrophobic	43	77	3	20	2							1017.4576	1016.4503	Out of the MS range
Modification of lipid A	I	UDP-4-(N-formylamino)-4-deoxy-L-arabinose	UDP-Ara4FN	C16156	--	Nucleotide	Hydrophilic	15	22	3	16	2							562.0475	561.0403	
O antigen biosynthesis (not in K-12)	VI	UDP-D-galacto-1,4-furanose	C03733	--	--	Nucleotide	Hydrophilic	15	24	2	17	2							566.0550	565.0478	
Cholanic acid biosynthesis	I	UDP-galactose	UDP-Gal	C00052	+	Nucleotide	Hydrophilic	15	24	2	17	2							566.0550	565.0478	
Peptidoglycan biosynthesis	I	UDP-GlcNAc-pyruvateolether	UDP-GlcNAcPyrEE	C04631	--	Nucleotide	Hydrophilic	20	29	3	19	2							677.0871	676.0798	
Cholanic acid biosynthesis	I	UDP-D-glucose	GDP-Glc	C00029	+	Nucleotide	Hydrophilic	15	24	2	17	2							566.0550	565.0478	
Cholanic acid biosynthesis	I	UDP-D-glucuronic acid	GDP-GlcA	C00167	+	Nucleotide	Hydrophilic	15	24	2	18	2							582.0499	581.0427	
KDO biosynthesis	I	UDP-3-O-(3-hydroxymyristoyl)glucosamine	UDP-HMyrGlc	C06022	--	Nucleotide	Hydrophobic	29	51	3	18	2							791.2643	790.2570	Neutral and/or hydrophobic
KDO biosynthesis	I	UDP-3-O-(3-hydroxymyristoyl)-N-acetylglucosamine	UDP-HMyrGlcNAc	C04738	--	Nucleotide	Hydrophobic	31	53	3	19	2							833.2749	832.2676	Neutral and/or hydrophobic
Modification of lipid A	I	UDP-4-ketopyranose	UDP-Ara4O	C16155	--	Nucleotide	Hydrophilic	14	19	2	16	2							533.0210	532.0137	
Modification of lipid A	I	Undecaprenyl phosphate-4-amino-4-deoxy-L-arabinose	Undecaprenyl-P-Ara4N	C16157	--	Anion	Hydrophobic	60	99	1	7	1							976.7159	975.7086	Neutral and/or hydrophobic
Isoopenoid biosynthesis	I	Undecaprenyldiphosphate	UPrPP	C03543	--	Nucleotide	Hydrophobic	55	92	7	2								926.6318	925.6246	Neutral and/or hydrophobic
Common antigen biosynthesis	I	Undecaprenyl-N-acetylglucosaminyl-N-acetylmannosaminuronate-4-acetamido-4,6-dideoxy-D-galactosepyrophosphate	UnGlcNAcManNAcAdDGalP	--	--	Nucleotide	Hydrophobic	79	129	3	22	2							1533.8543	1532.8470	Out of the MS range
Common antigen biosynthesis	I	Undecaprenyl-N-acetylglucosaminyl-N-acetylmannosaminuronatepyrophosphate	UnPGlcNAcManNAcNPP	--	--	Nucleotide	Hydrophobic	71	116	2	18	2							1346.7698	1345.7626	Out of the MS range
Common antigen biosynthesis	I	Undecaprenyl-N-acetyl-α-D-glucosaminylpyrophosphate	UnPrenylGlcNAcPP	C01289	--	Nucleotide	Hydrophobic	63	105	1	12	2							1129.7112	1128.7039	Out of the MS range
Common antigen biosynthesis	I	Undecaprenylphosphate	UnPreP	C00348	--	Nucleotide	Hydrophobic	55	91	4	1								846.6655	845.6582	Neutral and/or hydrophobic
Peptidoglycan biosynthesis	I	Undecaprenyl-pyrophosphoryl-MurNAc-(pentapeptide)-N-acetylglucosamine	UnPPMurNAcPentaPepNAc	C05898	--	Nucleotide	Hydrophobic	95	156	8	28	2							1919.0504	1918.0432	Out of the MS range
Salvage of pyrimidine	I	Uracil	C00106	+	Cation	Hydrophilic	4	4	2	2									112.0273	111.0346	
Polyamine biosynthesis	I	Urea	C00086	+	Cation	Hydrophilic	1	4	2	1									60.0324	61.0396	
Allantoin degradation	III	(S)-Ureidoglycolic acid	C00603	--	--	Anion	Hydrophilic	3	6	2	4								134.0328	133.0255	
Salvage of Ade, HypXan	I	Uric acid	C00366	+	Cation	Hydrophilic	5	4	4	3									168.0283	169.0356	
Salvage of pyrimidine	I	Uridine	C00299	+	Cation	Hydrophilic	9	12	2	6									244.0695	245.0768	
Pyrimidine biosynthesis	I	Uridine-5'-diphosphate	UDP	C00015	+	Nucleotide	Hydrophilic	9	14	2	12	2							404.0022	402.9949	
Pyrimidine biosynthesis	I	Uridine-5'-phosphate	UMP	C00105	+	Nucleotide	Hydrophilic	9	13	2	9	1							324.0359	323.0286	
Pyrimidine biosynthesis	I	Uridine-5'-triphosphate	UTP	C00075	+	Nucleotide	Hydrophilic	9	15	2	15	3							483.9685	482.9613	
Proto- and siroheme biosynthesis	I	Uroporphyrin III	C02469	--	--	Anion	Hydrophilic	40	36	4	16								828.2126	827.2054	
Proto- and siroheme biosynthesis	I	Uroporphyrinogen-III	UroPorgen-III	C01051	--	--	Anion	Hydrophilic	40	44	4	16							836.2752	835.2680	
Valine biosynthesis	I	L-Valine	Val	C00183	+	Cation	Hydrophilic	5	11	1	2								117.0790	118.0863	
Salvage of Ade, HypXan	I	Xanthine	C00385	+	Cation	Hydrophilic	5	4	4	2									152.0334	153.0407	
Salvage of Gua, Xan	I	Xanthosine	C01762	+	Cation	Hydrophilic	10	12	4	6									284.0757	285.0830	
Purine biosynthesis	I	Xanthosine-5-phosphate	XMP	C00655	+	Anion	Hydrophilic	10	13	4	9	1							364.0420	363.0347	
ITP, XTP dephosphorelation	IV	Xanthosine-5'-triphosphate	XTP	C00700	+	Nucleotide	Hydrophilic	10	15	4	15	3							523.9747	522.9674	
Xylose degradation	III	D-Xylose	C00181	+	Neutral	Hydrophilic	5	10	5										150.0528	--	Neutral and/or hydrophobic
L-Xylose transport	III	L-Xylose	C01510	--	--	Neutral	Hydrophilic	5	10	5									150.0528	--	Neutral and/or hydrophobic
Xylose degradation	III	D-Xylulose	C00310	+	Neutral	Hydrophilic	5	10	5										150.0528	--	Neutral and/or hydrophobic
L-Xylose degradation	III	L-Xylulose	C00312	--	--	Neutral	Hydrophilic	5	10	5									150.0528	--	Neutral and/or hydrophobic
Pentose phosphate pathway (non-oxidative)	I	D-Xylulose-5-phosphate	X5P	C00231	+	Anion	Hydrophilic	5	11	8	1								230.0192	229.0119	
Ascorbic acid degradation	III	L-Xylulose-5-phosphate	L-X5P	C03291	--	--	Anion	Hydrophilic	5	11	8	1							230.0192	229.0119	

a Classes; I, primary metabolism; II, degradation of primary metabolites; III, degradation of environmental compounds; IV, secondary or unconventional metabolism; V, pathway unknown; VI, intermediates in putative or in vitro reaction.

b Refer Kyoto Encyclopedia of Genes and Genomes (<http://www.genome.jp/kegg/>)

c Analytical mode is for CE-TOFMS analysis. See Experimental section in detail.

d See Experimental section.

Supplementary Table 2. Intracellular levels of *E. coli* metabolites in primary metabolisms.

Pathway	Class <sup>a</sup>	Metabolite	Abbreviation	Standard chemical	Analytical mode <sup>c</sup>	Molecular weight	<i>m/z</i> <sup>d</sup>	Map position <sup>e</sup>	Time after His shift down <sup>f</sup>				Description
									0 min	15 min	30 min	60 min	
Alanine biosynthesis	I	L-Alanine	Ala	+	Cation	89.0477	90.0550	C-3	0.1303	0.3287	0.3488	0.7112	
AppppA biosynthesis	I	P(1),P(4)-Bis(5'-adenosyl)tetraphosphate	AppppA	+	Nucleotide	836.0483	835.0410	A-1	0.0019	0.0016	0.0009	0.0008	
Arginine biosynthesis	I	L-Arginine	Arg	+	Cation	174.1117	175.1190	B-4	0.1622	0.2450	0.3125	1.0536	
Arginine biosynthesis	I	L-Argininosuccinic acid	ArgSuccinate	+	Cation	290.1226	291.1299	B-4	0.0057	0.0283	0.0229	0.0349	
Arginine biosynthesis	I	Carbamoylphosphate	Carbamoyl-P	+	Anion	140.9827	139.9754	C-4	ND	ND	ND	ND	
Arginine biosynthesis	I	L-Citrulline	Citrulline	+	Cation	175.0957	176.1030	B-4	0.0307	0.2098	0.1315	0.0062	
Arginine biosynthesis	I	<i>N</i> -Acetyl-L-glutamic acid	<i>N</i> -AcGlu	+	Cation	189.0637	190.0710	C-4	0.0034	0.0176	0.0338	0.0082	
Arginine biosynthesis	I	<i>N</i> -Acetylglutamylphosphate	<i>N</i> -AcGlu-P	+	Anion	269.0301	268.0228	C-4	UID	UID	UID	UID	
Arginine biosynthesis	I	<i>N</i> -Acetylglutamatesemialdehyde	<i>N</i> -AcGlu-semialdehyde	+	Anion	173.0688	172.0615	C-4	UID	UID	UID	UID	
Arginine biosynthesis	I	<i>N</i> - $\alpha$ -Acetylmorphine	<i>N</i> -AcOrn	+	Cation	174.1004	175.1077	C-4	0.9074	2.1800	0.1719	0.0091	
Arginine biosynthesis	I	L-Ornithine	Ornithine	+	Cation	132.0899	133.0972	C-4	0.0658	0.0373	0.0249	0.0043	
Asparagine biosynthesis	I	L-Asparagine	Asn	+	Cation	132.0535	133.0608	B-3	0.0817	0.0466	0.0871	0.2083	
Aspartic acid biosynthesis	I	L-Aspartic acid	Asp	+	Cation	133.0375	134.0448	B-3	0.1074	0.1057	0.1393	0.3255	
Biotin biosynthesis	I	7,8-Diaminononanoic acid	7,8DANA	+	Cation	188.1525	189.1598	C-2	0.0040	0.0068	0.0037	0.0044	
Biotin biosynthesis	I	8-Amino-7-oxononanoic acid	8A7ONA	+	Cation	187.1208	188.1281	C-2	UID	UID	UID	UID	
Biotin biosynthesis	I	Biotin	Biotin	+	Cation	244.0882	245.0954	D-2	0.1057	0.1339	0.1234	0.1201	
Biotin biosynthesis	I	Dethiobiotin	Dethiobiotin	+	Cation	214.1317	215.1390	C-2	0.0126	0.0135	0.0041	ND	
Biotin biosynthesis	I	Pimelic acid	Pimelic acid	+	Anion	160.0736	159.0663	C-2	ND	ND	ND	ND	
Biotin biosynthesis	I	Pimeloyl-CoA	Pimeloyl-CoA	+	Nucleotide	909.1782	908.1709	C-2	UID	UID	UID	UID	
Biotin biosynthesis	I	5-Adenosyl-4-methylthio-2-oxobutanoic acid	SA4MT2OBA	+	Cation	398.1134	398.1134	C-2	UID	UID	UID	UID	Including trinary sulfur
Biotin oxidation	I	<i>d</i> -Biotin- <i>d</i> -sulfoxide	BiotinSul	+	Cation	260.0831	261.0904	D-2	UID	UID	UID	UID	
cAMP biosynthesis	I	3',5'-Cyclicadenosine-5'-phosphate	cAMP	+	Nucleotide	329.0525	328.0452	A-1	0.0336	0.0449	0.0446	0.0468	
cGMP biosynthesis	I	3',5'-Cyclicguanosine-5'-phosphate	cGMP	+	Nucleotide	345.0474	344.0402	B-1	ND	ND	ND	ND	
Cholanic acid biosynthesis	I	$\alpha$ -D-Galactose-1-phosphate	Gal1P	+	Anion	260.0297	259.0224	C-1	0.0273	0.2024	0.1826	0.2002	
Cholanic acid biosynthesis	I	GDP-4-dehydro-6-deoxy-D-mannose	GDP-DDMan	+	Nucleotide	587.0666	586.0593	C-1	UID	UID	UID	UID	
Cholanic acid biosynthesis	I	GDP-L-fucose	GDP-fucose	+	Nucleotide	589.0822	588.0750	C-1	ND	ND	ND	ND	
Cholanic acid biosynthesis	I	UDP-D-glucose	UDP-Glc	+	Nucleotide	566.0550	565.0478	D-4		See UDP-Gal			
Cholanic acid biosynthesis	I	UDP-D-glucuronic acid	GDP-GlcA	+	Nucleotide	582.0499	581.0427	D-4	ND	ND	ND	ND	
Cholanic acid biosynthesis	I	GDP-mannose	GDP-Man	+	Nucleotide	605.0772	604.0699	C-1	ND	ND	ND	ND	
Cholanic acid biosynthesis	I	D-Mannose-1-phosphate	Man1P	+	Anion	260.0297	259.0224	C-1		See Gal1P			
Cholanic acid biosynthesis	I	D-Mannose-6-phosphate	Man6P	+	Anion	260.0297	259.0224	C-1		See Gal1P			
Cholanic acid biosynthesis	I	UDP-galactose	UDP-galactose	+	Nucleotide	566.0550	565.0478	D-4	0.3853	1.3488	1.2339	2.0746	
Chorismic acid biosynthesis	I	3-Deoxy-D-arabinoheptulosonate-7-phosphate	3DAH7P	+	Anion	288.0246	287.0174	B-2	0.0039	0.0155	0.0083	0.0060	
Chorismic acid biosynthesis	I	3-Dehydroquinate acid	3DQA	+	Anion	190.0500	189.0405	B-3	UID	UID	UID	UID	
Chorismic acid biosynthesis	I	3-Dehydroshikimate acid	3DSA	+	Anion	172.0372	171.0299	B-3	UID	UID	UID	UID	
Chorismic acid biosynthesis	I	5-Enolpyruvylshikimate-3-phosphate	5EPS3P	+	Anion	324.0246	323.0174	B-3	0.0278	0.0293	0.0359	0.0496	
Chorismic acid biosynthesis	I	Chorismic acid	Chorismic acid	+	Anion	226.0477	225.0405	A-3	ND	ND	ND	ND	
Chorismic acid biosynthesis	I	Shikimate-3-phosphate	S3P	+	Anion	254.0192	253.0119	B-3	UID	0.0076	0.0051	UID	
Chorismic acid biosynthesis	I	Shikimic acid	Shikimic acid	+	Anion	174.0528	173.0455	B-3	ND	ND	ND	ND	
CoA biosynthesis	I	D-4-Phosphopantothenic acid	4PPA	+	Nucleotide	299.0770	298.0697	D-2	UID	UID	UID	UID	
CoA biosynthesis	I	4-Phospho- <i>N</i> -pantothencysteine	4PPC	+	Nucleotide	402.0862	401.0789	D-2	UID	UID	UID	UID	
CoA biosynthesis	I	Coenzyme A	CoA	+	Nucleotide	767.1152	382.5503	D-2	0.2960	0.3911	0.1867	0.4736	Detected as divalent ion in MS
CoA biosynthesis	I	Dephospho-CoA	dePCoA	+	Nucleotide	687.1489	686.1416	D-2	0.0027	0.0024	0.0011	0.0025	
CoA biosynthesis	I	Pantetheine-4'-phosphate	P4P	+	Nucleotide	358.0964	357.0891	D-2	0.0065	0.0071	0.0053	0.0081	
Common antigen biosynthesis	I	dTDP-4-acetamido-4,6-dideoxy-D-galactose	dTDP-AADDGal	+	Nucleotide	589.1074	588.1001	D-2	0.0032	0.0059	0.0057	0.0122	
Common antigen biosynthesis	I	dTDP-D-fucosamine	dTDP-FAN	+	Nucleotide	547.0968	546.0896		UID	UID	UID	UID	
Common antigen biosynthesis	I	UDP- <i>N</i> -acetyl-D-mannosamine	UDP-ManNAc	+	Nucleotide	607.0816	606.0743			See UDP-GlcNAc			
Common antigen biosynthesis	I	UDP- <i>N</i> -acetyl-D-mannosaminouronic acid	UDP-ManNAcUA	+	Nucleotide	621.0608	620.0536		UID	UID	UID	UID	
Cysteine biosynthesis	I	<i>O</i> -Acetyl-L-serine	AcSer	+	Cation	147.0532	148.0604	C-3	0.0278	0.0173	0.0498	ND	
Cysteine biosynthesis	I	L-Cysteine	Cys	+	Cation	121.0198	122.0270	C-3	ND	ND	ND	ND	
dTDP-rhamnose biosynthesis	I	dTDP-4-dehydro-6-deoxy-D-glucose	dTDP-DDGlc	+	Nucleotide	546.0652	545.0579	C-1	UID	UID	UID	UID	
dTDP-rhamnose biosynthesis	I	dTDP-4-dehydro-6-deoxy-L-mannose	dTDP-DDMan	+	Nucleotide	546.0652	545.0579	D-1	UID	UID	UID	UID	
dTDP-rhamnose biosynthesis	I	dTDP-D-glucose	dTDP-Glc	+	Nucleotide	564.0758	563.0685	C-1	0.0034	0.0063	0.0051	0.0050	
dTDP-rhamnose biosynthesis	I	dTDP- $\alpha$ -L-rhamnose	dTDP-Rhm	+	Nucleotide	548.0808	547.0736	D-1	0.3977	0.5828	0.4606	0.5994	
Entner-Doudoroff pathway	I	2-Keto-3-deoxy-6-phosphogluconic acid	KDPGlcA	+	Anion	258.0141	257.0068	C-2	UID	UID	UID	UID	
Fatty acid biosynthesis	I	Malonyl-CoA	Malonyl-CoA	+	Nucleotide	853.1156	403.5556	B-3	ND	ND	ND	ND	Detected as acetyl-CoA in MS
Formyltetrahydrofolic acid biosynthesis	I	5,10-Methylene-THF	5,10MeL-THF	+	Cation	457.1710	458.1783	D-1	UID	UID	UID	UID	
Formyltetrahydrofolic acid biosynthesis	I	5,10-Methenyl-THF	5,10Me-THF	+	Cation	457.1704	457.1704	D-1	UID	UID	UID	UID	Including quarternary amine
Formyltetrahydrofolic acid biosynthesis	I	5-Methyl-THF	Me-THF	+	Cation	459.1866	460.1939	D-1	ND	ND	ND	ND	
Fravrin biosynthesis	I	2,5-Diamino-6-(ribosylamino)-4-(3H)-pyrimidinone-5'-phosphate	2,5DA6RA4P5P	+	Anion	353.0737	352.0664	B-2	UID	UID	UID	UID	
Fravrin biosynthesis	I	3,4-Dihydroxy-2-butanone-4-phosphate	3,4DH2B4P	+	Anion	184.0137	183.0064	A-2	UID	UID	UID	UID	
Fravrin biosynthesis	I	5-Amino-6-(5'-phosphoribosylamino)uracil	5A6-5'PRAU	+	Anion	354.0577	353.0504	B-2	UID	UID	UID	UID	
Fravrin biosynthesis	I	5-Amino-6-(5'-phosphoribitylamino)uracil	5A6-5'PRBU	+	Anion	356.0733	355.0660	B-2	UID	UID	UID	UID	
Fravrin biosynthesis	I	5-Amino-6-ribitylamino-2,4(1H,3H)-pyrimidinedione	5A6RbA2,4PD	+	Cation	276.1070	277.1143	A-2	UID	0.0019	0.0014	0.0027	
Fravrin biosynthesis	I	6,7-Dimethyl-8-(1-D-ribityl)lumazine	6,7DH8RBL	+	Anion	326.1226	325.1154	B-2	UID	UID	UID	UID	
Fravrin biosynthesis	I	Flavinadeninedinucleotide (oxidized form)	FAD	+	Nucleotide	785.1571	391.5713	B-2	0.0011	0.0013	0.0007	0.0007	Detected as divalent ion in MS
Fravrin biosynthesis	I	Flavinadeninedinucleotide (reduced form)	FADH <sub>2</sub>	+	Nucleotide	787.1728	786.1655	A-2	UID	UID	UID	UID	
Fravrin biosynthesis	I	Flavinmononucleotide (oxidized form)	FMN	+	Nucleotide	456.1046	455.0973	B-2	0.0062	0.0088	0.0030	0.0056	
Fravrin biosynthesis	I	Flavinmononucleotide (reduced form)	FMNH <sub>2</sub>	+	Nucleotide	458.1203	457.1130	B-2	UID	UID	UID	UID	
Fravrin biosynthesis	I	Riboflavin	Riboflavin	+	Cation	376.1383	377.1456	B-2	ND	ND	ND	ND	
Glutamic acid biosynthesis	I	L-glutamic acid	Glu	+	Cation	147.0532	148.0604	C-4	3.2033	8.8863	7.8141	9.3902	
Glutamine biosynthesis	I	L-Glutamine	Gln	+	Cation	146.0691	147.0764	C-4	0.2763	0.1228	0.3678	0.5476	
Glutathione biosynthesis	I	$\gamma$ -Glutamylcysteine	GluCys	+	Cation	250.0623	251.0696	C-3	0.0096	0.0210	0.0147	0.0118	
Glutathione biosynthesis	I	Glutathione (reduced form)	GSH	+	Cation	307.0838	308.0911	D-3	5.6358	2.9306	1.5100	7.3357	
Glutathione biosynthesis	I	Glutathione (oxidized form)	GSSG	+	Cation	612.1520	307.0833	D-3	0.0236	0.0187	0.0196	0.0487	Detected as divalent ion in MS
Glutathionylspermidine metabolism	I	Glutathionylspermidine	GSH-spermidine	+	Cation	434.2311	435.2384	D-3	0.0007	UID	UID	UID	
Glycine biosynthesis	I	Glycine	Gly	+	Cation	75.0320	76.0393	C-2	0.1901	0.2894	0.2619	0.4944	
Glycogen biosynthesis	I	ADP-D-glucose	ADP-Glc	+	Nucleotide	589.0822	588.0750	C-2	ND	ND	ND	ND	
Glycogen biosynthesis	I	$\alpha$ -D-Glucose-1-phosphate	G1P	+	Anion	260.0297	259.0224	C-2	ND	ND	ND	ND	
Glycolysis (Embden-Meyerhof-Parnas)	I	1,3-Diphosphateglyceric acid	1,3-DPG	+	Anion	265.9593	264.9520	C-2	ND	ND	ND	ND	
Glycolysis (Embden-Meyerhof-Parnas)	I	2-Phosphoglyceric acid	2-PG	+	Anion	185.9929	184.9857	C-3		See 3PG			
Glycolysis (Embden-Meyerhof-Parnas)	I	3-Phosphoglyceric acid	3-PG	+	Anion	185.9929	184.9857	C-3	0.1180	0.1270	0.0759	0.0764	
Glycolysis (Embden-Meyerhof-Parnas)	I	Dihydroxyacetonephosphate	DHAP	+	Anion	169.9980	168.9908	C-2	ND	0.0150	0.0136	0.0012	
Glycolysis (Embden-Meyerhof-Parnas)	I	D-Fructose-1,6-diphosphate	F1,6P	+	Anion	339.9961	338.9888	C-2	0.0129	0.2166	0.2631	0.0555	
Glycolysis (Embden-Meyerhof-Parnas)	I	D-Fructose-6-phosphate	F6P	+	Anion	260.0297	259.0224	C-2	ND	ND	ND	ND	
Glycolysis (Embd													

Menaquinone biosynthesis	I	1,4-Dihydroxy-2-naphthoic acid	1,4DHNaphA	+	Anion	204.0423	203.0350	A-4	ND	ND	ND	ND
Menaquinone biosynthesis	I	Isochorismic acid	Isochorismic acid	-	Anion	226.0477	225.0405	A-3	UID	UID	UID	UID
Menaquinone biosynthesis	I	O-Succinylbenzoic acid	OSucBA	-	Anion	222.0528	221.0455	A-3	UID	UID	UID	UID
Menaquinone biosynthesis	I	O-Succinylbenzoyl-CoA	OSucB-CoA	-	Nucleotide	971.1575	970.1502	A-4	UID	UID	UID	UID
Menaquinone biosynthesis	I	2-Succinyl-6-hydroxy-2,4-cyclohexadiene-1-carboxylic acid	SucCycHexCA	-	Anion	240.0634	239.0561	A-3	UID	UID	UID	UID
Methionine biosynthesis	I	5-Methyltetrahydropteroyltri-L-glutamic acid	5MHTGlu	-	Cation	640.2453	641.2525	A-3	UID	UID	UID	UID
Methionine biosynthesis	I	Cystathionine	Cystathionine	-	Cation	222.0674	223.0747	A-3	0.0091	0.0120	0.0060	UID
Methionine biosynthesis	I	Homocysteine	HomoCys	-	Cation	135.0354	136.0427	A-3	0.0054	0.0066	0.0080	0.0048
Methionine biosynthesis	I	L-Methionine	Met	+	Cation	149.0511	150.0583	A-4	0.0371	0.0724	0.0654	0.0605
Methionine biosynthesis	I	O-Succinyl-L-homoserine	SucHomoSer	+	Cation	219.0743	220.0816	A-3	0.0379	0.0714	0.0613	0.0079
Methionine biosynthesis	I	Tetrahydropteroyltri-L-glutamic acid	THPTGlu	-	Cation	626.2296	627.2369	A-3	UID	UID	UID	UID
Methionine oxidation	I	L-Methionine sulfoxide	MetSFx	+	Cation	165.0460	166.0532	A-4	0.0017	0.0032	0.0032	0.0031
Methylglyoxal pathway	I	D-Lactic acid	D-Lactic acid	+	Anion	90.0317	89.0244					See Lactic acid
Methylglyoxal pathway	I	S-Lactoylglutathione	SL-GSH	+	Cation	379.1049	380.1122	D-2	0.0076	0.0092	0.0075	0.0144
Modification of lipid A	I	4-Amino-4-deoxy-L-arabinose	Ara4N	-	Cation	149.0688	150.0761		UID	UID	UID	UID
Modification of lipid A	I	UDP-4-(N-formylamino)-4-deoxy-L-arabinose	UDP-Ara4FN	-	Nucleotide	562.0475	561.0403		UID	UID	UID	UID
Modification of lipid A	I	UDP-4-amino-4-deoxy-L-arabinose	UDP-Ara4N	-	Nucleotide	534.0526	533.0453		UID	UID	UID	UID
Modification of lipid A	I	UDP-4-ketopyranose	UDP-Ara4O	-	Nucleotide	533.0210	532.0137		UID	UID	UID	UID
Molybdopterin biosynthesis	I	Molybdopterin formA	Mol-form A	-	Anion	326.0290	325.0218		UID	UID	UID	UID
Molybdopterin biosynthesis	I	Molybdopterin formA-GMP	Mol-form A-GMP	-	Nucleotide	671.0765	670.0692		UID	UID	UID	UID
Molybdopterin biosynthesis	I	Molybdopterin-guaninedinucleotide	MolGDN	-	Nucleotide	738.0441	737.0368		UID	UID	UID	UID
Molybdopterin biosynthesis	I	Molybdopterin	Molybdopterin	-	Anion	395.0123	394.0050		UID	UID	UID	UID
Molybdopterin biosynthesis	I	Precursor-Z	Precursor-Z	-	Cation	345.0474	346.0547		UID	UID	UID	UID
NAD biosynthesis	I	Deamido-NAD	Deamido-NAD	+	Nucleotide	665.1004	663.0859	B-4	ND	0.0008	0.0007	0.0008
NAD biosynthesis	I	Iminoaspartic acid	Iminoaspartic acid	-	Cation	131.0219	132.0291	B-3	UID	UID	UID	UID
NAD biosynthesis	I	Nicotinamideadeninedinucleotide (reduced form)	NAD <sup>+</sup>	+	Nucleotide	664.1164	662.1019	B-4	0.4564	0.6664	0.5548	0.6989
NAD biosynthesis	I	Nicotinamideadeninedinucleotide (oxidized form)	NADH	+	Nucleotide	665.1248	664.1175	B-4	0.0032	0.0038	0.0027	0.0023
NAD biosynthesis	I	Nicotinamideadeninedinucleotidephosphate (reduced form)	NADP <sup>+</sup>	+	Nucleotide	744.0827	742.0682	B-4	0.1046	0.1730	0.1382	0.1543
NAD biosynthesis	I	Nicotinamideadeninedinucleotidephosphate (oxidized form)	NADPH	+	Nucleotide	745.0911	743.5383	B-4	0.0086	0.0151	0.0113	0.0092
NAD biosynthesis	I	Nicotinatenucleotide	Nicotinatenucleotide	+	Nucleotide	336.0484	334.0339	B-4	ND	ND	ND	ND
NAD biosynthesis	I	Quinolinic acid	Quinolinic acid	+	Anion	167.0219	166.0146	B-3	ND	ND	ND	ND
Pantothenic acid biosynthesis	I	2-Dehydropanoic acid	ZDHPA	-	Anion	146.0579	145.0506	D-3	0.0150	0.0090	0.0150	0.0072
Pantothenic acid biosynthesis	I	β-Alanine	β-Ala	+	Cation	89.0477	90.0550	D-3	ND	ND	ND	ND
Pantothenic acid biosynthesis	I	L-Pantoic acid	Pantoic acid	-	Anion	148.0736	147.0663	D-3	UID	UID	UID	UID
Pantothenic acid biosynthesis	I	Pantothenic acid	Pantothenic acid	+	Anion	219.1107	218.1034	D-2	0.0207	0.0134	0.0139	0.0216
Pentose phosphate pathway (non-oxidative)	I	D-Erythrose-4-phosphate	E4P	+	Anion	200.0086	199.0013	B-2	0.0014	0.0058	0.0057	0.0024
Pentose phosphate pathway (non-oxidative)	I	D-Ribose-5-phosphate	R5P	+	Anion	230.0192	229.0119	B-2	ND	0.0061	0.0089	0.0069
Pentose phosphate pathway (non-oxidative)	I	D-Sedoheptulose-7-phosphate	S7P	-	Anion	290.0403	289.0330	B-2	0.0100	0.0308	0.0293	0.0299
Pentose phosphate pathway (non-oxidative)	I	D-Xylulose-5-phosphate	X5P	+	Anion	230.0192	229.0119	B-2	ND	ND	ND	ND
Pentose phosphate pathway (oxidative)	I	6-Phospho-D-gluconic acid	6-PG	+	Anion	276.0246	275.0174	B-2	0.0014	0.0159	0.0157	0.0122
Pentose phosphate pathway (oxidative)	I	D-Glucono-Δ-lactone-6-phosphate	GlcL6P	-	Anion	258.0141	257.0068	B-2	UID	UID	UID	UID
Pentose phosphate pathway (oxidative)	I	D-Ribulose-5-phosphate	Ru5P	+	Anion	230.0192	229.0119	B-2	0.0214	0.0080	0.0116	0.0145
Peptidoglycan biosynthesis	I	D-Alanyl-D-alanine	AlaAla	+	Cation	160.0848	161.0921	D-2	0.2194	0.1643	0.1755	0.5799
Peptidoglycan biosynthesis	I	L-alanyl-D-glutamyl-meso-A2pm	AlaGluA2pm	-	Cation	390.1751	391.1823	D-2	UID	UID	0.0035	0.0065
Peptidoglycan biosynthesis	I	D-Alanine	D-Ala	+	Cation	89.0477	90.0550					See Ala
Peptidoglycan biosynthesis	I	D-Glutamic acid	D-Glu	+	Cation	147.0532	148.0604					See Glu
Peptidoglycan biosynthesis	I	UDP-N-acetylmuramoyl-L-alanyl-D-glutamic acid	UDP-GlcNAcMurAlaGlu	-	Nucleotide	879.1824	878.1751		UID	UID	UID	UID
Peptidoglycan biosynthesis	I	UDP-GlcNAc-pyruvateenolether	UDP-GlcNAcPyrEE	-	Nucleotide	677.0871	676.0798		UID	UID	UID	UID
Peptidoglycan biosynthesis	I	UDP-N-acetylmuramic acid	UDP-MurNAcA	-	Nucleotide	679.1027	678.0954	D-2	0.0682	0.0912	0.0630	0.0548
Peptidoglycan biosynthesis	I	UDP-N-acetylmuramoyl-L-alanine	UDP-MurNAcAla	-	Nucleotide	750.1398	749.1325		UID	UID	UID	UID
Phenylalanine biosynthesis	I	L-Phenylalanine	Phe	+	Cation	165.0790	166.0863	A-3	0.1028	0.4073	0.3727	0.7846
Phenylalanine biosynthesis	I	Phenylpyruvic acid	Phenylpyruvic acid	+	Anion	164.0473	163.0401	A-3	ND	0.0161	0.0098	0.0069
Polyamine acetylation	I	N <sup>1</sup> -Acetylspermidine	N1AcSpermidine	-	Cation	187.1685	188.1757	A-4	0.0354	0.0276	0.0172	0.0352
Polyamine acetylation	I	N <sup>1</sup> -Acetylspermine	N1AcSpermine	+	Cation	244.2263	245.2336	A-4	ND	ND	ND	ND
Polyamine acetylation	I	Spermine	Spermine	+	Cation	202.2157	203.2230	A-4	ND	ND	ND	ND
Polyamine biosynthesis	I	Agmatine	Agmatine	+	Cation	130.1218	131.1291	B-4	0.0014	0.0126	0.0125	0.0081
Polyamine biosynthesis	I	S-Adenosylmethionine	dAdoMet	+	Cation	355.1552	355.1552	A-4	UID	0.0111	UID	UID
Polyamine biosynthesis	I	5-Methylthioadenosine	MTA	+	Cation	297.0896	298.0968	A-4	0.1223	0.2122	0.2002	0.3119
Polyamine biosynthesis	I	Putrescine	Putrescine	+	Cation	88.1000	89.1073	B-4	1.5761	1.2554	1.2431	1.2192
Polyamine biosynthesis	I	Spermidine	Spermidine	+	Cation	145.1579	146.1652	A-4	0.0229	0.0334	0.0351	0.0482
Polyamine biosynthesis	I	Urea	Urea	+	Cation	60.0324	61.0396	B-4	0.6000	0.6969	0.4909	0.4880
ppGpp biosynthesis	I	Guanosine-5'-diphosphate,3'-diphosphate	ppGpp	+	Nucleotide	602.9570	601.9497	B-1	ND	0.0163	0.0047	0.0116
ppGpp biosynthesis	I	Guanosine-3'-diphosphate-5'-triphosphate	pppGpp	-	Nucleotide	682.9233	681.9161	B-1	UID	UID	UID	UID
Prephenic acid biosynthesis	I	Prephenic acid	Prephenic acid	+	Anion	226.0477	225.0405	A-3	ND	ND	ND	ND
Proline biosynthesis	I	L-Glutamate-5-phosphate	Glu-5-P	-	Anion	227.0195	226.0122	C-4	UID	UID	UID	UID
Proline biosynthesis	I	L-Glutamate-γ-semialdehyde	Glu-semialdehyde	-	Cation	131.0582	132.0655	C-4	UID	UID	UID	UID
Proline biosynthesis	I	L-Proline	Pro	+	Cation	115.0633	116.0706	B-4	0.0245	0.1245	0.0520	0.0531
Proline biosynthesis	I	L-Δ <sup>1</sup> -pyrroline-5-carboxylic acid	Pyrrroline-5-carboxylate	+	Anion	113.0477	112.0404	C-4	ND	ND	ND	ND
Proto- and siroheme biosynthesis	I	5-Aminolevulinic acid	5-Aminolevulinic acid	+	Cation	131.0582	132.0655	C-4	ND	ND	ND	ND
Proto- and siroheme biosynthesis	I	Coproporphyrinogen III	CoPorgen III	-	Anion	660.3159	659.3086		UID	UID	UID	UID
Proto- and siroheme biosynthesis	I	Glutamate-1-semialdehyde	GluSA	-	Cation	131.0582	132.0655	C-4	UID	UID	UID	UID
Proto- and siroheme biosynthesis	I	Hydroxymethylbilane	HMB	-	Anion	854.2858	853.2785		UID	UID	UID	UID
Proto- and siroheme biosynthesis	I	Protoporphyrin IX	Por IX	+	Anion	562.2580	561.2507		ND	ND	ND	ND
Proto- and siroheme biosynthesis	I	Porphobilinogen	Porphobilinogen	+	Cation	226.0954	227.1026	C-4	0.0077	0.0084	0.0104	0.0084
Proto- and siroheme biosynthesis	I	Precorrin-1	Precorrin-1	-	Anion	850.2909	849.2836		UID	UID	UID	UID
Proto- and siroheme biosynthesis	I	Precorrin-2	Precorrin-2	-	Anion	864.3065	863.2993		UID	UID	UID	UID
Proto- and siroheme biosynthesis	I	Protoheme IX	Protoheme IX	-	Anion	614.1616	613.1544	C-4	0.8815	0.4759	0.2597	0.8773
Proto- and siroheme biosynthesis	I	Protoporphyrinogen IX	Protoporphyrinogen IX	-	Anion	564.2737	563.2664		UID	UID	UID	UID
Proto- and siroheme biosynthesis	I	S-Adenosylhomocysteine	SAHC	+	Cation	384.1216	385.1289	C-4	ND	ND	ND	ND
Proto- and siroheme biosynthesis	I	Siroheme	Siroheme	-	Anion	916.2102	915.2029	C-4	UID	UID	UID	UID
Proto- and siroheme biosynthesis	I	Sirohydrochlorin	Sirohydrochlorin	-	Anion	862.2909	861.2836		UID	UID	UID	UID
Proto- and siroheme biosynthesis	I	Uroporphyrinogen-III	UroPorgen-III	-	Anion	836.2752	835.2680		UID	UID	UID	UID
Proto- and siroheme biosynthesis	I	Uroporphyrin III	Uroporphyrin III	-	Anion	828.2126	827.2054		UID	UID	UID	UID
PRPP biosynthesis	I	5-Phosphoribosyl-diphosphate	PRPP	+	Nucleotide	389.9518	388.9445	B-2	ND	0.0252	0.0121	0.0137
PRPP biosynthesis	I	D-Ribose-1,5-diphosphate	R1,5P	-	Nucleotide	309.9855	308.9782	B-2	0.0157	0.0295	0.0203	0.0089
Purine biosynthesis	I	Adenosine-5'-diphosphate	ADP	+	Nucleotide	427.0294	426.0221	A-1	0.2736	0.4401	0.3575	0.2055
Purine biosynthesis	I	Aminoimidazole carboxamide ribonucleotide	AICAR	+	Nucleotide	338.0628	337.0555	A-1	ND	0.0013	0.0080	0.0100
Purine biosynthesis	I	5-Aminoimidazole ribonucleotide	AIR	-	Nucleotide	295.0569	294.0497	A-2	UID	UID	UID	UID
Purine biosynthesis	I	Adenine-5'-phosphate	AMP	+	Nucleotide	347.0631	346.0558	A-1	0.0769	0.0643	0.0607	0.0523
Purine biosynthesis	I	Adenylosuccinic acid	ASA	+	Nucleotide	449.0584	448.0511	A-1	ND	ND	ND	ND
Purine biosynthesis	I	Adenosine-5'-triphosphate	ATP	+	Nucleotide	506.9958	505.9885	A-1	0.5021	2.2443	1.5756	0.7624
Purine biosynthesis	I	5'-Phosphoribosyl-4-carboxy-5-aminoimidazole	CAIR	-	Nucleotide	339.0468	338.0395	A-1	UID	UID	UID	UID
Purine biosynthesis	I	Deoxyadenosine-5'-diphosphate	dADP	+	Nucleotide	411.0345	410.0272	A-1	0.0313	0.0293	0.0316	0.0236
Purine biosynthesis	I	Deoxyadenine-5'-triphosphate	dATP	+	Nucleotide	491.0008	489.9936	A-1	0.0519	0.1308	0.1210	0.0844
Purine biosynthesis	I	Phosphoribosylformamidocarboxamide	FAICAR	-	Nucleotide	366.0577	365.0504	A-1	UID	UID	UID	UID
Purine biosynthesis	I	5-Phosphoribosyl-N-formylglycineamide	FGAR	-	Nucleotide	313.0675	312.0602	A-2	0.0028	0.0044	0.0017	UID
Purine biosynthesis	I	5'-Phosphoribosyl-N-formylglycineamide	FGAR	-	Nucleotide	314.0515	313.0442	A-2	UID	0.0019	0.0036	0.0015
Purine biosynthesis	I	5-Phosphoribosylglycineamide	GAR	-	Nucleotide	286.0566	285.0493	A-2	UID	UID	UID	UID
Purine biosynthesis	I	Guanosine-5'-diphosphate	GDP	+	Nucleotide	443.0243	442.0171	B-1	0.0630	0.0938	0.1106	0.0921
Purine biosynthesis	I	Guanine-5'-phosphate	GMP	+	Nucleotide	363.0580	362.0507	B-1	0.0055	0.0058	0.0078	0.0064
Purine biosynthesis	I	Guanosine-5'-triphosphate	GTP	+	Nucleotide	521.9828	520.9756	B-1	0.0682	0.2711	0.3277	0.2215
Purine biosynthesis	I	Inosine-5'-phosphate	IMP	+	Nucleotide	348.0471	347.0398	A-1	ND	ND	ND	ND
Purine biosynthesis	I	N <sup>5</sup> -Carboxyaminoimidazole ribonucleotide	N5-CAIR	-	Nucleotide	338.0389	337.0317	A-2	UID	UID	UID	UID
Purine biosynthesis	I	5-Phosphoribosylamine	PRA	-	Nucleotide	229.0351	228.0279	A-2	UID	UID	UID	UID
Purine biosynthesis	I	5'-Phosphoribos										

Salvage of Ade, HypXan	I	Adenine	Adenine	+	Cation	135.0545	136.0618	A-1	0.0056	0.0073	0.0094	0.0053	
Salvage of Ade, HypXan	I	Adenosine	Adenosine	+	Cation	267.0968	268.1040	A-1	0.0077	0.0243	0.0221	0.0046	
Salvage of Ade, HypXan	I	Deoxyadenosine	dAdenosine	+	Cation	251.1018	252.1091	A-1	ND	ND	ND	ND	
Salvage of Ade, HypXan	I	Deoxyinosine	dInosine	+	Cation	252.0859	253.0931	A-1	ND	ND	ND	ND	
Salvage of Ade, HypXan	I	Hypoxanthine	Hypoxanthine	+	Cation	136.0385	137.0458	A-1	0.0844	0.0368	0.0387	0.0517	
Salvage of Ade, HypXan	I	Inosine	Inosine	+	Cation	268.0808	269.0880	A-1	0.0290	0.0072	0.0129	0.0157	
Salvage of Ade, HypXan	I	Uric acid	Uric acid	+	Cation	168.0283	169.0356	B-1	ND	ND	ND	ND	
Salvage of Ade, HypXan	I	Xanthine	Xanthine	+	Cation	152.0334	153.0407	B-1	0.0189	ND	ND	ND	
Salvage of Gua, Xan	I	Deoxyguanosine	dGuanosine	+	Cation	267.0968	268.1040	B-1	0.0077	0.0243	0.0234	0.0046	
Salvage of Gua, Xan	I	Deoxyribose-1-phosphate	dR1P	+	Anion	214.0242	213.0170	D-3	ND	ND	ND	ND	
Salvage of Gua, Xan	I	Guanine	Guanine	+	Cation	151.0494	152.0567	B-1	0.0316	0.0037	0.0074	0.0154	
Salvage of Gua, Xan	I	Guanosine	Guanosine	+	Cation	283.0917	284.0989	B-1	0.0253	0.0103	0.0214	0.0127	
Salvage of Gua, Xan	I	D-Ribose-1-phosphate	R1P	-	Anion	230.0192	229.0119	B-2	UID	UID	UID	UID	
Salvage of Gua, Xan	I	Xanthosine	Xanthosine	+	Cation	284.0757	285.0830	B-1	ND	ND	ND	ND	
Salvage of pyridoxal-5'-phosphate	I	Pyridoxal	Pyridoxal	+	Cation	167.0582	168.0655		ND	ND	ND	ND	
Salvage of pyridoxal-6'-phosphate	I	Pyridoxamine	Pyridoxamine	+	Cation	168.0899	169.0972		0.0016	0.0231	0.0221	0.0239	
Salvage of pyridoxal-7'-phosphate	I	Pyridoxamine-5'-phosphate	PX5P	+	Anion	248.0562	247.0489		0.0174	0.0117	0.0193	0.0220	
Salvage of pyridoxal-8'-phosphate	I	Pyridoxine	Pyridoxine	+	Cation	169.0739	170.0812		ND	ND	ND	ND	
Salvage of pyrimidine	I	Cytidine-5'-phosphate	UMP	+	Nucleotide	323.0519	322.0446	D-4	0.0254	0.0239	0.0222	0.0456	
Salvage of pyrimidine	I	Cytidine	Cytidine	+	Cation	243.0855	244.0928	D-4	ND	ND	ND	ND	
Salvage of pyrimidine	I	Cytosine	Cytosine	+	Cation	111.0433	112.0505	D-4	0.0090	0.0029	0.0026	0.0044	
Salvage of pyrimidine	I	Deoxycytidine	dCyt	+	Cation	227.0906	228.0979	D-3	ND	ND	ND	ND	
Salvage of pyrimidine	I	Deoxyuridine	dUri	+	Cation	228.0746	229.0819	D-3	ND	ND	ND	ND	
Salvage of pyrimidine	I	Thymidine	Thymidine	+	Cation	242.0903	243.0975	D-3	ND	ND	ND	ND	
Salvage of pyrimidine	I	Thymine	Thymine	+	Cation	126.0429	127.0502	D-3	0.0027	ND	ND	ND	
Salvage of pyrimidine	I	Uracil	Uracil	+	Cation	112.0273	113.0346	D-4	ND	ND	ND	ND	
Salvage of pyrimidine	I	Uridine	Uridine	+	Cation	244.0695	245.0768	D-4	ND	ND	ND	ND	
SAM biosynthesis	I	S-Adenosyl-L-methionine	SAM	+	Cation	399.1451	399.1451	A-4	0.0420	0.0693	0.0671	0.1181	Including trinary sulfur
Serine biosynthesis	I	3-Phosphohydroxypyruvic acid	3PHPA	-	Anion	183.9773	182.9700	C-3	UID	UID	UID	UID	
Serine biosynthesis	I	3-Phosphoserine	3PSer	+	Anion	185.0089	184.0017	C-3	ND	ND	0.0017	ND	
Serine biosynthesis	I	L-Serine	Ser	+	Cation	105.0426	106.0499	C-3	0.1112	0.2028	0.1328	0.1815	
Sulfuric acid assimilation	I	Adenosine-5'-phosphosulfate	APS	+	Nucleotide	427.0199	426.0126	C-2	0.0182	0.0711	0.0534	0.0255	
Sulfuric acid assimilation	I	Adenosine-3',5'-diphosphate	pAp	+	Nucleotide	427.0294	426.0221	D-2	0.0177	0.0675	0.0526	0.0246	
Sulfuric acid assimilation	I	3'-Phosphoadenosine-5'-phosphosulfate	PAPS	-	Nucleotide	506.9862	505.9790	C-2	UID	UID	UID	UID	
TCA cycle	I	2-Oxoglutaric acid	2-OG	+	Anion	146.0215	145.0142	C-4	ND	0.0911	0.0423	0.0303	
TCA cycle	I	cis-Aconitic acid	cis-Aconitic acid	+	Anion	174.0164	173.0092	C-3	ND	0.0057	0.0064	0.0006	
TCA cycle	I	Citric acid	Citric acid	+	Nucleotide	192.0270	191.0197	C-3	0.0763	0.6989	0.5342	0.2005	
TCA cycle	I	Fumaric acid	Fumaric acid	+	Anion	116.0110	115.0037	B-4	0.0128	0.0872	0.0481	0.0368	
TCA cycle	I	Isocitric acid	Isocitric acid	+	Nucleotide	192.0270	191.0197	C-4	ND	ND	ND	ND	
TCA cycle	I	Malic acid	Malic acid	-	Anion	134.0215	133.0142	B-3	0.0197	0.2072	0.1314	0.1180	
TCA cycle	I	Succinic acid	Succinic acid	+	Anion	118.0266	117.0193	B-4	0.0720	0.6073	0.3211	0.2371	
TCA cycle	I	Succinyl-CoA	SuccCoA	+	Nucleotide	867.1313	432.5584	C-4	0.0009	0.0076	0.0021	0.0021	Detected as divalent ion in MS
Tetrahydrofolic acid biosynthesis	I	4-Amino-4-deoxychorismic acid	ADCA	-	Cation	225.0637	226.0710	C-1	UID	UID	UID	UID	
Tetrahydrofolic acid biosynthesis	I	2-Amino-4-hydroxy-6-hydroxymethyl-7,8-dihydropteridinediphosphate	AHMeDHPPD	-	Nucleotide	355.0083	354.0010	C-1	0.0011	0.0012	0.0007	UID	
Tetrahydrofolic acid biosynthesis	I	7,8-Dihydrofolic acid	DHFA	+	Cation	443.1553	444.1626	D-1	ND	ND	ND	ND	
Tetrahydrofolic acid biosynthesis	I	Dihydroneopterin-3'-triphosphate	DHMTP	-	Nucleotide	494.9958	493.9885	B-1	UID	UID	UID	UID	
Tetrahydrofolic acid biosynthesis	I	7,8-Dihydroneopterin	DHN	+	Cation	255.0968	256.1040	C-1	ND	ND	ND	ND	
Tetrahydrofolic acid biosynthesis	I	Dihydroneopterinphosphate	DHNMP	-	Nucleotide	335.0631	334.0558	C-1	UID	UID	UID	UID	
Tetrahydrofolic acid biosynthesis	I	7,8-Dihydroneopterin-3'-triphosphate	DHNTP	-	Nucleotide	494.9958	493.9885	B-1	UID	UID	UID	UID	
Tetrahydrofolic acid biosynthesis	I	7,8-Dihydroptericoic acid	DHPA	-	Cation	314.1127	315.1200	C-1	UID	UID	UID	UID	
Tetrahydrofolic acid biosynthesis	I	6-Hydroxymethyldehydropterin	HMeDHP	-	Cation	195.0756	196.0829	C-1	UID	UID	UID	UID	
Tetrahydrofolic acid biosynthesis	I	N <sup>10</sup> -Formyl-THF	N10-THF	-	Cation	473.1659	474.1732	D-1	UID	UID	UID	UID	
Tetrahydrofolic acid biosynthesis	I	p-Aminobenzoic acid	PABA	+	Cation	137.0477	138.0550	C-1	ND	ND	ND	ND	
Thiamine biosynthesis	I	4-Amino-5-hydroxymethyl-2-methylpyrimidinepyrophosphate	4A5HMe2MePyrPP	-	Nucleotide	299.0072	298.0000	D-1	0.0014	0.0021	0.0021	0.0019	
Thiamine biosynthesis	I	4-Methyl-5-(β-hydroxyethyl)thiazole	4Me5BHEthThiazole	+	Cation	143.0405	144.0478		ND	ND	ND	ND	
Thiamine biosynthesis	I	4-Methyl-5-(β-hydroxyethyl)thiazolephosphate	4Me5BHEthThiazoleP	-	Anion	223.0068	221.9995		UID	UID	UID	UID	
Thiamine biosynthesis	I	Hydroxymethylpyrimidine	HMePyr	-	Cation	139.0746	140.0818		UID	UID	UID	UID	
Thiamine biosynthesis	I	Hydroxymethylpyrimidinephosphate	HMePyrP	-	Anion	219.0409	218.0336		UID	UID	UID	UID	
Thiamine biosynthesis	I	Thiamine	Thiamine	+	Cation	265.1123	265.1123	D-1	0.2570	0.2594	0.2030	0.2280	Including quarternary amine
Thiamine biosynthesis	I	Thiaminediphosphate	ThiamineDP	+	Nucleotide	425.0450	423.0304	D-1	0.3180	0.4812	0.4164	0.4198	Including quarternary amine
Thiamine biosynthesis	I	Thiaminephosphate	ThiamineP	+	Cation	345.0786	345.0786	D-1	0.3903	0.6529	0.5103	0.5588	Including quarternary amine
Threonine biosynthesis	I	O-Phospho-L-homoserine	P-HomoSer	-	Anion	199.0246	198.0173	A-3	0.0061	0.0138	0.0091	UID	
Threonine biosynthesis	I	L-Threonine	Thr	+	Cation	119.0582	120.0655	A-4	2.4406	0.2364	0.2374	0.3449	
Trehalose biosynthesis	I	Trehalose-6-phosphate	Tre6P	+	Anion	422.0825	421.0753	C-1	ND	ND	ND	ND	
Tryptophan biosynthesis	I	Anthraniic acid	Anthraniic acid	+	Cation	137.0477	138.0550	A-2	ND	ND	ND	ND	
Tryptophan biosynthesis	I	1-(o-Carboxyphenylamino)-1'-deoxyribulose-5'-phosphate	CPADRP	-	Nucleotide	349.0563	348.0490	A-2	UID	UID	UID	UID	
Tryptophan biosynthesis	I	Indole-3-glycerolphosphate	IG-P	-	Nucleotide	287.0559	286.0486	A-2	UID	UID	UID	UID	
Tryptophan biosynthesis	I	Indole	Indole	+	Cation	117.0578	118.0651	A-2	ND	ND	ND	ND	
Tryptophan biosynthesis	I	N-(5'-Phosphoribosyl)anthranilic acid	PRAnth	-	Nucleotide	349.0563	348.0490	A-2	UID	UID	UID	UID	
Tryptophan biosynthesis	I	L-Tryptophan	Trp	+	Cation	204.0899	205.0972	A-2	0.0338	0.0519	0.0521	0.0761	
Tyrosine biosynthesis	I	p-Hydroxyphenylpyruvic acid	HPP	+	Anion	180.0423	179.0350	A-3	ND	0.0167	ND	0.0085	
Tyrosine biosynthesis	I	L-Tyrosine	Tyr	+	Cation	181.0739	182.0812	A-3	0.2976	0.6528	0.6505	1.2055	
Ubiquinone biosynthesis	I	p-Hydroxybenzoic acid	PHBA	+	Anion	138.0317	137.0244	A-3	0.0072	0.0102	0.0130	0.0184	
UDP-N-acetylglucosamine biosynthesis	I	D-Glucosamine-1-phosphate	Glc-1P	-	Anion	259.0457	258.0384	C-2				See Glc-6P	
UDP-N-acetylglucosamine biosynthesis	I	D-Glucosamine-6-phosphate	Glc-6P	+	Anion	259.0457	258.0384	C-2	0.0321	0.0263	0.0359	0.0326	
UDP-N-acetylglucosamine biosynthesis	I	N-Acetylglucosamine-1-phosphate	GlcNac-P	+	Anion	301.0563	300.0490	C-2	0.0011	ND	ND	ND	
UDP-N-acetylglucosamine biosynthesis	I	UDP-N-acetyl-D-glucosamine	UDP-GlcNac	+	Nucleotide	607.0816	606.0743	C-2	0.1931	0.3081	0.2426	0.1477	
Valine biosynthesis	I	2,3-Dihydroxyisovaleric acid	2,3-DIV	-	Anion	134.0579	133.0506	C-3	0.0233	0.0562	0.0536	0.0139	
Valine biosynthesis	I	2-Acetoacetic acid	2-Ac	-	Anion	132.0423	131.0350	C-3	UID	0.0255	0.0050	0.0111	
Valine biosynthesis	I	2-Ketoisovaleric acid	2-KIV	+	Anion	116.0473	115.0401	C-3	ND	0.0245	ND	0.0011	
Valine biosynthesis	I	L-Valine	Val	+	Cation	117.0790	118.0863	C-3	0.1214	0.4426	0.3240	0.5089	
Acetylglucosamine dissimilation	II	N-Acetyl-D-mannosamine-6-phosphate	ManNac6P	-	Anion	301.0563	300.0490		UID	UID	UID	UID	
Acetylglucosamine dissimilation	II	N-Acetylneuraminic acid	NeuNac	+	Anion	309.1060	308.0987	D-2	0.0035	0.0198	0.0165	0.0290	
Arginine degradation	II	N <sup>2</sup> -Succinyl-L-arginine	N2SucArg	-	Cation	274.1277	275.1350	B-4	0.0014	0.0011	0.0015	0.0222	
Arginine degradation	II	N <sup>2</sup> -Succinylglutamic acid	N2SucGlu	-	Cation	247.0692	248.0765	B-4	UID	0.0030	0.0019	0.0026	
Arginine degradation	II	N <sup>2</sup> -Succinylglutamate-5-semialdehyde	N2SucGluSA	-	Cation	233.0899	234.0972	B-4	UID	UID	UID	UID	
Arginine degradation	II	N <sup>2</sup> -Succinylornithine	N2SucOrn	-	Cation	232.1059	233.1132	B-4	0.0373	0.0236	0.0161	0.0116	
Glucosamine degradation	II	N-Acetyl-D-glucosamine-6-phosphate	NacGlcNP	+	Anion	301.0563	300.0490		ND	ND	ND	ND	
Histidine degradation	II	Imidazole lactic acid	Im-lactate	-	Cation	156.0535	157.0608	B-1	0.0044	0.0008	UID	UID	
Histidine degradation	II	Imidazolepyruvic acid	Im-pyruvic acid	-	Cation	154.0378	155.0451	B-1	UID	UID	UID	UID	
Lysine degradation	II	Cadaverine	Cadaverine	+	Cation	102.1157	103.1230		0.0026	0.0053	0.0081	0.0072	
Methylmalonyl pathway	II	D-Methylmalonyl-CoA	D-MeMal-CoA	+	Nucleotide	867.1313	432.5584	A-4	ND	0.0055	0.0009	0.0012	Detected as divalent ion in MS
Methylmalonyl pathway	II	L-Methylmalonyl-CoA	L-MeMal-CoA	-	Nucleotide	867.1313	432.5584	A-4		See D-MeMal-CoA			Detected as divalent ion in MS
Peptidoglycan turnover	II	Anhydro-N-acetylmuramic acid	AHMurNac	-	Cation	275.1005	276.1078		UID	UID	UID	UID	
Peptidoglycan turnover	II	L-Alanyl-γ-D-glutamyl-meso-diaminopimelyl-D-alanine	AlaGluDAPAla	-	Cation	433.1809	434.1882		UID	UID	UID	UID	
Peptidoglycan turnover	II	L-Alanyl-γ-D-glutamyl-diaminopimelic acid	L-Ala-D-Glu-Dap	-	Cation	309.1437	310.1510		UID	UID	UID	UID	
Putrescine degradation	II	4-Aminobutyraldehyde	4ABA	-	Cation	87.0684	88.0757		UID	UID	UID	UID	
Ribosephosphate degradation	II	Deoxyribose-5-phosphate	dR5P	+	Anion	214.0242	213.0170		ND	ND	ND	ND	
S-Adenosylhomocysteine catabolism	II	S-D-Ribose-L-homocysteine	RibHomoCys	-	Cation	267.0777	268.0849	C-4	0.0300	0.0241	0.0172	0.0096	
Short fatty acid degradation	II	Acetoacetyl-CoA	Acetoacetyl-CoA	+	Nucleotide	851.1363	850.1291		ND	ND			

**Supplementary Fig. 1. Metabolome profile of *E. coli* after histidine downshift.**

