Supporting Information for

In Situ Metabolic Profiling of Single Cells by Laser Ablation Electrospray Ionization Mass Spectrometry

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Table S1. Tentative peak assignments in the mass spectrum of a single unpigmented epidermal cell from *A. cepa* bulb.

Metabolites	**Formula**	$m/z_{\text{calc.}}$	$m/z_{\text{meas.}}$	**Δm (mDa)**
pyruvaldehyde	$C_3H_4O_2$ $(+H^+)$	73.0290	73.0188	-10.2
thioacrolein	C_3H_4S $(+H^+)$	73.0112	73.0188	7.6
5-aminoimidazole	$C_3H_5N_3$ $(+H^+)$	84.0562	84.0452	-11.0
furanone	$C_4H_4O_2$ $(+H^+)$	85.0290	85.0310	2.0
2-aminoacrylic acid	$C_3H_5NO_2$ $(+H^+)$	88.0399	88.0426	2.7
proline	$C_5H_9NO_2$ $(+H^+)$	116.0712	116.0747	3.5
2-oxohexa-4,5-cyclopropyl-5-enoic acid	$C_6H_6O_3$ $(+H^+)$	127.0395	127.0440	4.5
thymine	$C_5H_6N_2O_2$ $(+H^+)$	127.0508	127.0440	-6.8
5-oxoproline	$C_5H_7NO_3$ $(+H^+)$	130.0504	130.0527	2.3
p-aminobenzoic acid and/or vitamin L1	$C_7H_7NO_2$ $(+H^+)$	138.0555	138.0493	-6.2
glutamine and/or 3-ureido-isobutyric acid	$C_5H_{10}N_2O_3$ $(+H^+)$	147.0770	147.0811	4.1
histidine and/or bacimethrin	$C_6H_9N_3O_2$ $(+H^+)$	156.0773	156.0833	6.0
allylcysteine	$C_6H_{11}NO_2S$ $(+H^+)$	162.0589	162.0678	8.9
acetylhomoserine, α-aminoadipic acid	$C_6H_{11}NO_4$ $(+H^+)$	162.0766	162.0678	-8.8
phenylalanine	$C_9H_{11}NO_2$ $(+H^+)$	166.0868	166.0914	4.6
arginine [b]	$C_6H_{14}N_4O_2$ $(+H^+)$	175.1195	175.1202	0.7
alliin	$C_6H_{11}NO_3S$ $(+H^+)$	178.0538	178.0606	6.8
galactosamine	$C_6H_{13}NO_5$ $(+H^+)$	180.0872	180.0815	-5.7
tyrosine and/or α-aminooxy-β-phenylpropionic acid	$C_9H_{11}NO_3$ $(+H^+)$	182.0817	182.0807	-1.0
monosaccharide [a]	$C_6H_{12}O_6$ $(+K^+)$	219.0271	219.0269	-0.2
arginino-succinic acid	$C_{10}H_{18}N_4O_6$ $(+H^+)$	291.1305	291.1224	-8.1
glucosan or dextrin unit	$(C_6H_{10}O_5)_2$ $(+H^+)$ [c]	325.1135	325.1068	-6.7
disaccharide [a,b]	$C_{12}H_{22}O_{11}$ $(+K^+)$	381.0799	381.0801	0.2
trisaccharide [a,b]	$C_{18}H_{32}O_{16}$ $(+K^+)$	543.1328	543.1311	-1.7
heptasaccharide [a]	$C_{42}H_{72}O_{36}$ $(+H^+ + K^+)$	596.1759	596.1743	-1.6
oligosaccharide (DP 8 units) [a, c]	$C_{48}H_{82}O_{41}$ $(+H_2O + H^+ + K^+)$	686.2076	686.2177	10.1
tetrasaccharide [a,b]	$C_{24}H_{42}O_{21}$ $(+K^+)$	705.1856	705.1854	-0.2
oligosaccharide (DP 9 units) [a, c]	$C_{54}H_{92}O_{46}$ $(+H_2O + H^+ + K^+)$	767.2340	767.2286	-5.4
oligosaccharide (DP 10 units) [a, c]	$C_{60}H_{102}O_{51}$ $(+H_2O + H^+ + K^+)$	848.2604	848.2584	-2.0
pentasaccharide [a]	$C_{30}H_{52}O_{26}$ $(+K^+)$	867.2384	867.2381	-0.3
hexasaccharide [a, b]	$C_{36}H_{62}O_{31}$ $(+K^+)$	1029.2913	1029.2922	0.9

[a]Other adduct, and/or quasi-molecular, and/or cluster ions of the chemical species were also observed in the LAESI mass spectra.

[b]These ions were used as internal mass standards.

[c]DP = Degree of polymerization.

Table S2. Tentative peak assignments in the mass spectrum of a single epidermal cell from *N. pseudonarcissus* bulb.

Metabolites	Formula	$m/z_{calc.}$	$m/z_{meas.}$	Δm (mDa)
5-aminoimidazole	$C_3H_5N_3$ ($+H^+$)	84.0562	84.0468	-9.4
furanone	$C_4H_4O_2$ ($+H^+$)	85.0290	85.0295	0.5
proline	$C_5H_9NO_2$ ($+H^+$)	116.0712	116.0725	1.3
succinic acid	$C_4H_6O_4$ ($+H^+$)	119.0344	119.0243	-10.1
homoserine	$C_4H_9NO_3$ ($+H^+$)	120.0661	120.0809	14.8
3-methylene-indolenine	$C_5H_7NO_3$ ($+H^+$)	130.0504	130.0548	4.4
asparagine	$C_4H_8N_2O_3$ ($+H^+$)	133.0613	133.0638	2.5
glutamine and/or 3-ureido-isobutyric acid	$C_5H_{10}N_2O_3$ ($+H^+$)	147.0770	147.0799	2.9
histidine and/or bacimethrin	$C_6H_9N_3O_2$ ($+H^+$)	156.0773	156.0804	3.1
gallic acid	$C_7H_6O_5$ ($+H^+$)	171.0293	171.0203	-9
arginine [b]	$C_6H_{14}N_4O_2$ ($+H^+$)	175.1195	175.1218	2.3
caranine and/or crinine and/or vittatine	$C_{16}H_{17}NO_3$ ($+H^+$)	272.1287	272.1302	1.5
norpluviine	$C_{16}H_{19}NO_3$ ($+H^+$)	274.1443	274.1423	-2
galanthamine and/or mesembrenone and/or pluviine	$C_{17}H_{21}NO_3$ ($+H^+$)	288.1600	288.1467	-13.3
crinamine and/or haemanthamine	$C_{17}H_{19}NO_4$ ($+H^+$)	302.1392	302.1290	-10.2
homolycorine	$C_{18}H_{21}NO_4$ ($+H^+$)	316.1549	316.1512	-3.7
galanthine and/or lycorenine and/or papyramine	$C_{18}H_{23}NO_4$ ($+H^+$)	318.1705	318.1665	-4
disaccharides [a, b]	$C_{12}H_{22}O_{11}$ ($+K^+$)	381.0799	381.0710	-8.9
trisaccharides [a, b]	$C_{18}H_{32}O_{16}$ ($+K^+$)	543.1328	543.1394	6.6
tetrasaccharide	$C_{24}H_{42}O_{21}$ ($+H_2O+K^+$)	723.1961	723.1855	-10.6

[a]Other adduct, and/or quasi-molecular, and/or cluster ions of the chemical species were also observed in the LAESI mass spectra.

[b]These ions were used as internal mass standards.

Table S3. Comparative list of tentative peak assignments for the LAESI mass spectra of the colorless and pigmented cells in the onion bulb epidermis. The purple background in the table indicates ions found exclusively in the pigmented cells.

Metabolites	Formula	Purple	Colorless
furanone	$C_4H_4O_2$ ($+H^+$)	85.0268	85.0262
2-aminoacrylic acid	$C_3H_5NO_2$ ($+H^+$)	88.0388	88.0370
thymine and/or 2-oxohexa-4,5-cyclopropyl-5-enoic acid	$C_5H_6N_2O_2$ ($+H^+$) and/or $C_6H_6O_3$ ($+H^+$)	127.0374	127.0370
oxoproline	$C_5H_7NO_3$ ($+H^+$)	130.0546	130.0469
glutamine and/or 3-ureido-isobutyric acid	$C_5H_{10}N_2O_3$ ($+H^+$)	147.0766	147.0753
alliin	$C_6H_{11}NO_3S$ ($+H^+$)	178.0515	178.0525
galactosamine	$C_6H_{13}NO_5$ ($+H^+$)	180.0869	180.0870
monosaccharide [a]	$C_6H_{12}O_6$ ($+K^+$)	219.0259	219.0258
cyanidin and/or kaempferol	$C_{15}H_{11}O_6^+$	287.0593	-
quercetin	$C_{15}H_{10}O_7$ ($+H^+$)	303.0520	-
glucosan and/or dextrin unit [a]	$(C_6H_{10}O_5)_2$ ($+H^+$)	325.1122	325.1128
disaccharide [a]	$C_{12}H_{22}O_{11}$ ($+K^+$)	381.0822	381.0819
dityrosine	$C_{18}H_{20}N_2O_6$ ($+Na^+$)	383.1148	383.1148
disaccharide + quercetin glucoside	$C_{12}H_{22}O_{11}$ ($+K^+$) + $C_{21}H_{20}O_{12}$ ($+H^+$)	423.0884	-
cyanidin glucoside and/or kaempferol glucoside [a]	$C_{21}H_{21}O_{11}^+$	449.1164	-
peonidin glucoside	$C_{22}H_{23}O_{11}^+$	463.1262	-
quercetin glucoside [a]	$C_{21}H_{20}O_{12}$ ($+H^+$)	465.1082	
adenylyl aminoadipic acid	$C_{16}H_{23}N_6O_{10}P$ ($+H^+$)	491.1235	-
trisaccharide + quercetin glucoside	$C_{18}H_{32}O_{16}$($+K^+$) + $C_{21}H_{20}O_{12}$ ($+H^+$)	504.1145	-
cyanidin malonyl glucoside	$C_{24}H_{23}O_{14}^+$	535.1132	-
peonidin malonoyl glucoside	$C_{25}H_{25}O_{14}^+$	549.1303	-
trisaccharide	$C_{18}H_{32}O_{16}$ ($+H_2O+K^+$)	-	561.1495
cyanidin malonoyl acetoyl glucoside	$C_{26}H_{25}O_{15}^+$	577.1219	-
quercetin rutinoside, quercetin glucoside rhamnoside	$C_{27}H_{30}O_{16}$ ($+H^+$)	611.1697	-
cyanin, cyanidin diglucoside	$C_{27}H_{31}O_{16}^+$	611.1697	-
quercetin diglucoside [a]	$C_{27}H_{30}O_{17}$ ($+H^+$)	627.1638	-
cyanidin malonyl diglucoside	$C_{30}H_{33}O_{19}^+$	697.1754	-
tetrasaccharide	$C_{24}H_{42}O_{21}$ ($+H_2O+K^+$)	723.1995	723.2080
peonidin glucoside + quercetin	$C_{22}H_{23}O_{11}^+ + C_{15}H_{10}O_7$	765.1505	-
quercetin triglucoside	$C_{33}H_{40}O_{22}$ ($+H^+$)	789.2043	-
2 disaccharides + quercetin glucoside [a]	$C_{12}H_{22}O_{11} + C_{21}H_{20}O_{12}$ ($+Na^+$)	829.2299	-
2 disaccharides + quercetin diglucoside	$C_{12}H_{22}O_{11} + C_{27}H_{30}O_{17}$ ($+Na^+$)	991.2538	-
quercetin triglucoside + quercetin glucoside	$C_{33}H_{40}O_{22} + C_{21}H_{20}O_{12}$ ($+H^+$)	1253.3040	-
quercetin diglucoside + quercetin diglucoside [a]	$(C_{27}H_{30}O_{17})_2$ ($+H^+$)	1253.3040	-

[a]Other adduct, and/or quasi-molecular, and/or cluster ions of the chemical species were also observed in the LAESI mass spectra.