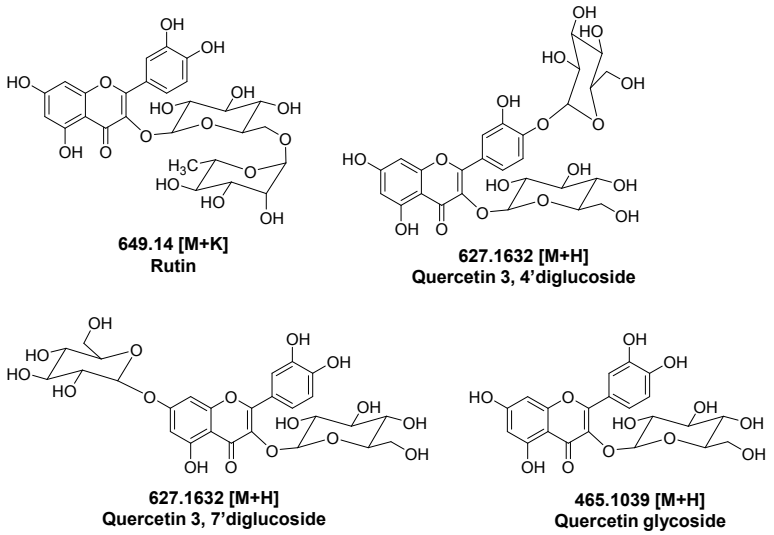
Electronic Supplementary Material (ESI) for Analyst.

Supporting Information for Local Collection, Reaction and Analysis with Theta Pipette Emitters

Scheme 1: Chemical Structures of neutral flavonoid molecules detected post-protonation of *A. cepa* cytoplasm



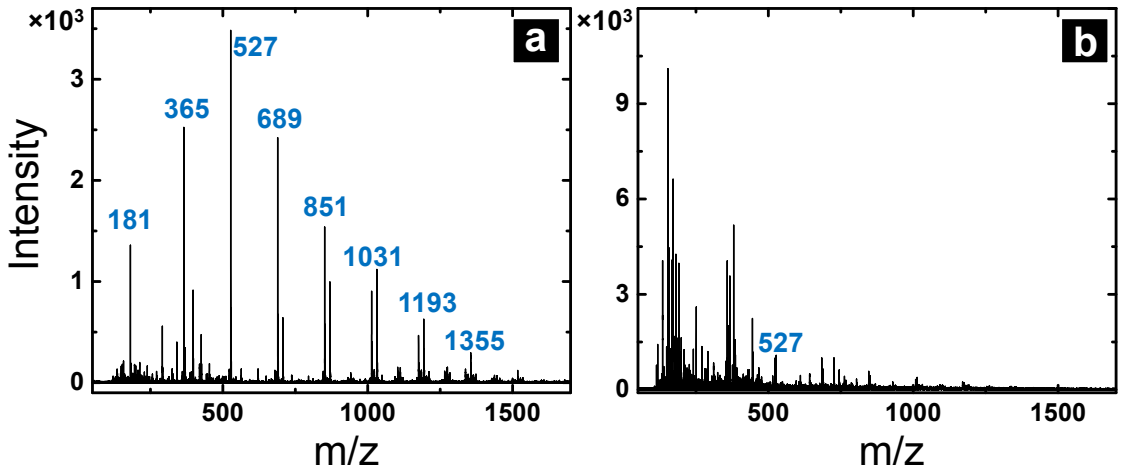


Figure S1. (a) Mass spectrum of dextran solution sampled and electrosprayed from a pipette before (a) and after (b) acid catalyzed degradation.

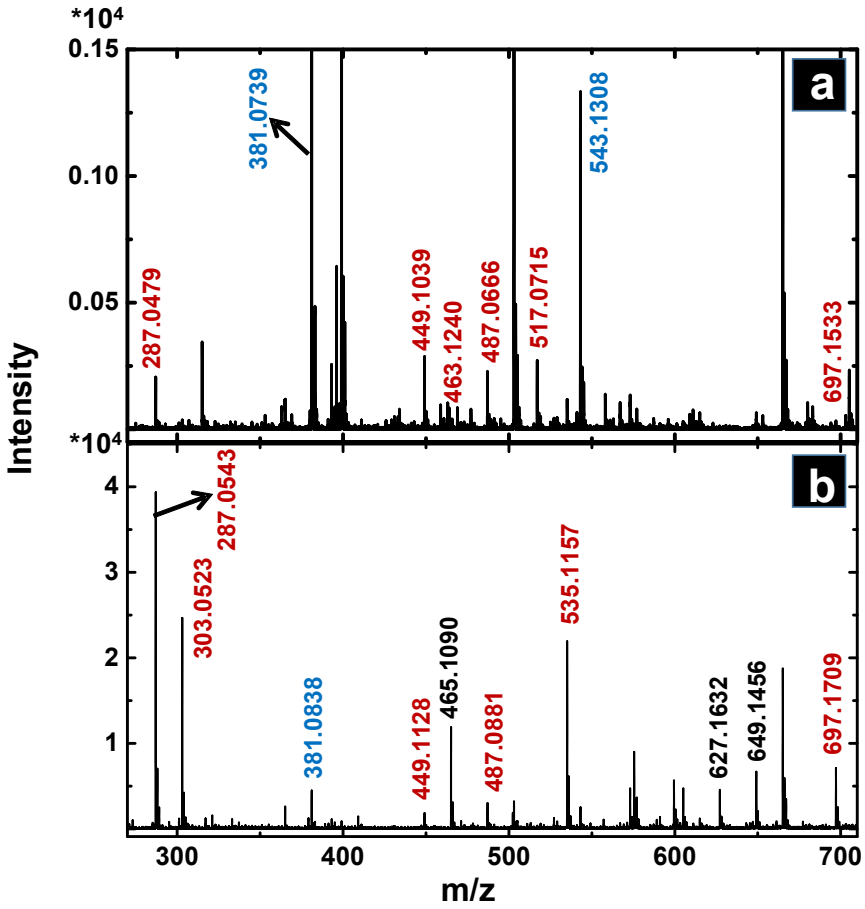


Figure S2. (a) Native Allium cepa cytoplasm and (b) after degradation of oligosaccharides. Peaks labelled in red correspond to anthocyanins, in blue are hexose oligosaccharides and in black are lipids.

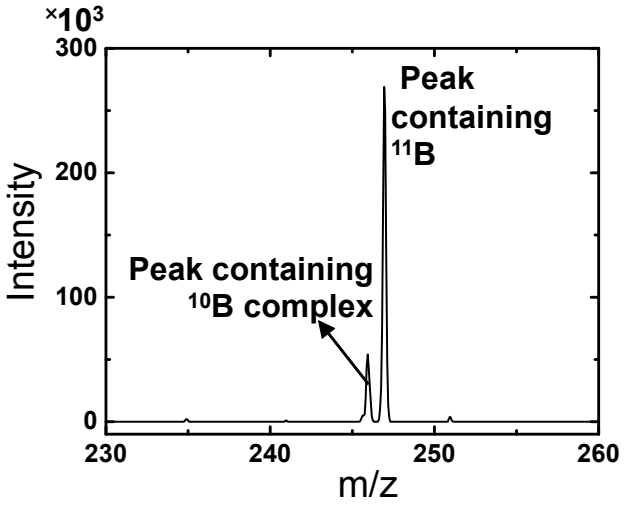


Figure S3. Mass spectrum showing unique isotopic pattern displayed by incorporation of one boron molecule. The peak shown here corresponds to PBA-monosaccharide complex zoomed-in from **Figure 3a**

When derivatization of oligosaccharides obtained from single *A. cepa* cells were attempted with a pipette having the conductive barrel of the pipette filled with pH 9 solution of 10 μM PBA, the mass spectrum was dominated by peaks corresponding to dimers and trimers of PBA as shown below. Although, peaks corresponding to S-B complexes, for example m/z 265, could be isolated in the ion trap and subjected to tandem MS as shown in **Figure S2**, their intensities were low compared to PBA dimer and trimer peaks.

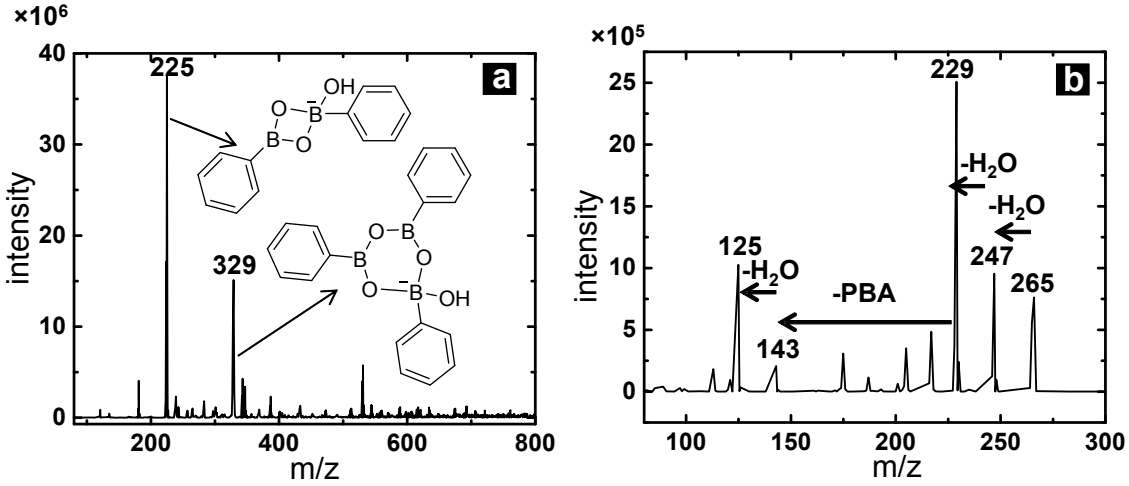


Figure S4. (a) Mass spectrum of sample collected from single *A. cepa* cell was subjected to PBA derivatization. The conductive barrel in this study was filled with pH 9 solution of 10 μM PBA to enable S-B complexation. The peak at m/z 265 corresponding to monosaccharide-PBA complex

was isolated and subjected to tandem MS. (b) The MS showing the fragments obtained from m/z 265.

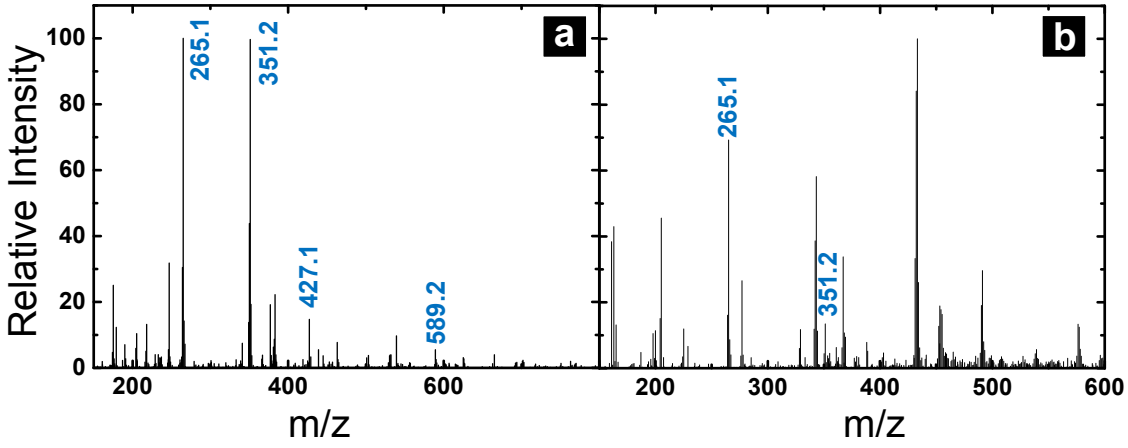


Figure S5. (a) Mass spectrum of *A. cepa* bulk extract containing hexose oligosaccharides that was subjected to phenylboronic acid (PBA) complexation at pH 9. (b) Mass spectrum of 10 µM solution of galactose which was subjected PBA complexation at pH 9. Peak at 265 is monosaccharide-PBA complex, at 351 is bis-monosaccharide-PBA complex, at 427 is disaccharide-PBA complex and at 589 is trisaccharide-PBA complex.

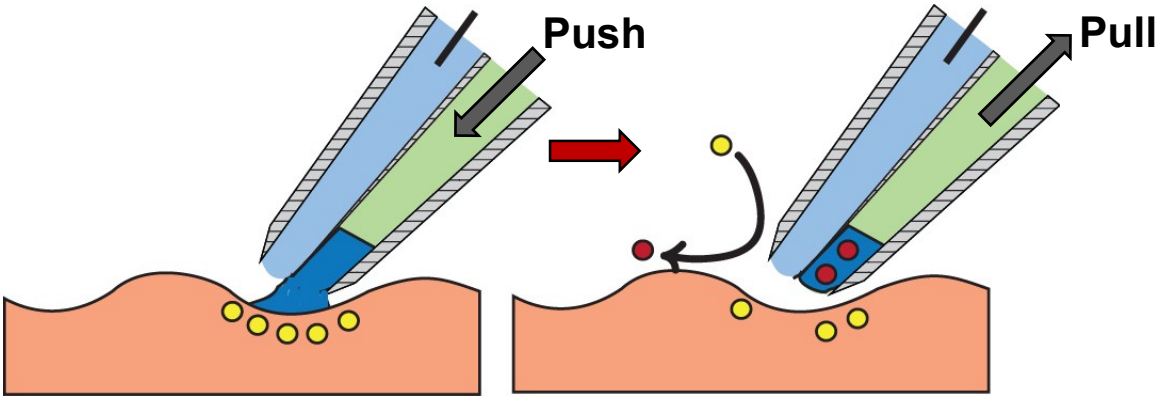


Figure S6: Schematic showing the strategy for local reactions on flat tissue sections such as *P. aeruginosa* biofilms.

Table S1. Tentative Peak assignments of saccharides and flavonoid from *Allium cepa* epidermal cell in Figure 1

Assignment	Exact mass	Observed mass	Δ ppm
Cyanidin	287.0515	287.0498	6.9
Delphinidin/quercetin+H^+	303.0505	303.0508	1
Disaccharide+K^+	381.0799	381.0727	18.8
Cyanidin glucoside	449.1006	449.1039	7.3
Quercetin glucoside+H^+	465.1033	465.1034	0.2
Cyanidin malonyl glucoside	535.1087	535.1102	2.8
Trisaccharide+K^+	543.1328	543.1308	3.6
Cyanidin malonyl acetoyl glucoside	577.1193	577.1322	22.3
Quercetin diglycoside+H	627.1561	627.1728	20.5
Rutin+K	649.1170	649.1456	44
Cyanidin malonyl diglucoside	697.1616	697.1626	1.4
Tetrasaccharide+K^+	705.1875	705.1875	0

Table S2. Tentative peak assignments for metabolites and rhamnolipids in *P. aeruginosa* biofilms

Assignment	Observed mass	Exact mass	Δ ppm
Pyocyanice (PYO)	211.0832	211.0871	18.4
2-heptyl-4-hydroxyquinolone (HHQ)	244.1650	244.1701	20.1
2-heptyl-3-hydroxy-4-quinolone (PQS)	260.1608	260.1650	16.1
2-nonyl-4-hydroxyquinolone (NHQ)	272.1972	272.2014	14.6
C11:db-2-undecyl-4-hydroxyquinoline (UHQ)	298.2140	298.2170	10.0
2-undecyl-4-hydroxyquinoline *N*-oxide (UQNO)	314.2017	314.2120	32.2
Rhamnolipid (Rha) C10-C10+K	543.3212	543.2935	50.1
Rha-Rha C10-C10+K	689.3389	689.3514	18.1