Electronic Supplementary Material (ESI) for Analyst.

Supp. Table 1. Signals and chemical classes identified from the direct analysis of the EB using DART MS and laser desorption ionization MS.

Supp. Fig. 1. (**A-F**) DART MS spectra measured from six replicate EBs analyzed on the same sample strip at 300 ˚C. The spectra are qualitatively similar and contain the major signals corresponding to cVA, deacetylated cVA, CH503, and deacetylated CH503. Some quantitative variation is evident - e.g., in **B** and **F**, the intensity of the FA signal at m/z 257.248 is comparable or higher than that of cVA and CH503. Unless otherwise indicated, ions are detected as $[M+H]^+$.

Supp. Fig. 2. DART MS analysis of cVA and CH503 synthetic standards shows a loss of acetate from both molecules and loss of water from CH503. The patterns of pheromone decomposition are consistent with those observed from direct analysis of EB tissue. Signals found in both synthetic standards and direct tissue analysis are labeled in blue. Analysis was performed at 300 ˚C.

Supp. Fig. 3. Effect of ion source temperature on synthetic tributyrin [(4:0/ 4:0/ 4:0)-TAG] and diolein [(18:1/ 18:1)-DAG]. (**A**) The loss of C4:0 acyl groups from tributyrin significantly increases with temperature; *p=0.03-0.04; **: p=0.0051; ***: p=0.0002-0.0007; ****: p<0.0001, Kruskal-Wallis. **(B)**. DAGs are detected as dehydrated ions at every temperature tested; **: p=0.0023, Kruskal-Wallis. For both graphs, each point represents the mean ± S.D, n=5-7.

Supp. Fig. 4. Representative spectra from EBs washed with various solvents; NS: no solvent. Mass signals corresponding to cVA, CH503, deacetylated fragments, fatty acids (FA), diacylglycerides (DAGs) and triacylglycerides (TAGs) are labeled.

Supp. Fig. 5. The abundance of fatty acids (FA) in solvent-only controls and EBs treated with solvents measured at 250 ˚C. The FA levels were similar between solvent-only and solvent-treated EBs in ethanol and chloroform/ MeOH (CM) conditions. Levels of FAs in untreated EBs or EBs treated with MeOH or hexane could be distinguished from baseline levels. For all graphs, bars indicate mean ± S.E.M; Mann-Whitney test, n=4-6.