Supporting Information to:

Metabolic Profiling of *Echinacea* Genotypes and a Test of Alternative Taxonomic Treatments

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Supporting Information for Materials and Methods

Plant materials

Seed samples of the 40 accessions were soaked for 24 hours in a 1 mM solution of ethephon to overcome dormancy and promote rapid germination [1]. After soaking, seeds were transferred to clear plastic boxes with blotters moistened with distilled water. Germination boxes were held at 4 °C for four weeks and then transferred to germination chambers maintained at a constant 25 °C with 14 hours of illumination per day. Three-week-old seedlings were transferred into 20-cm pots in a growing medium consisting of 50% Canadian Peat Moss, 40% Perlite, and 10% mineral soil and grown under ambient light in a greenhouse at 22–25 °C with daily watering. Pots were arranged on a single greenhouse bench in a completely randomized design generated from a random-digits table [2]. Fresh roots were harvested from 6-month-old plants. To standardize plant materials with respect to possible diurnal metabolic variation, harvests took place between 9 a.m. and 10 a.m. Harvested roots were thoroughly washed and rinsed with distilled water and were immediately chopped and ground to a fine powder in liquid N_2 in a mortar and pestle and stored in liquid N_2 until extraction. Each accession was analyzed in triplicate on independently extracted plant samples from three individual plants.

Compound quantification

A mixture of alkamides **8**/**9** (97% purity) was purchased (Phytolab). Alkamides **2**, **8**, **10**, **11**, **12**, **13**, and **14**, Chen alkamide, and ketone **22** were synthesized in-house. Analysis of the ^{1}H-NMR and mass spectra of these synthesized compounds reflected purity >90%. In the absence of standards for selected compounds, alkamides **1**, **3**, **4**, **5**, **7**, **15**, **16**, and **17** and

ketone **24** were identified by HPLC fractionation coupled with GC–MS analysis. Determination of the relative abundance of compounds was carried out by calculating UV response relative to the internal standard. 7-Hydroxy-(E)-*N*-isobutylundeca-2-ene-8,10-diynamide ($C_{15}H_{21}O_2$) has been found suitable to use as an internal standard for lipophilic metabolites because it has not been found in *Echinacea* plants and does not co-elute with any other observed metabolites. By adding an internal standard prior to extraction, we were able to quantify both known and unknown metabolites by calculating UV response relative to the internal standard. Specifically, of the 43 lipophilic metabolites, alkamides **12**, **13**, **14**, **16**, and **17**, ketones **22** and **24**, unknowns **B1**–**B6**, and unknowns **1**–**9** were determined at A210 nm with respect to the internal standard. Alkamides **1**, **2**, **3**, **4**, **7**, **10**, and **11**, Chen amide, unknowns **A1**–**A5** (all with similar UV spectra), and unknown **10** were determined at A260 nm with respect to the internal standard, by using a relative-response factor derived from reference standard alkamide **2**, to correct for absorbance differences between these metabolites and the internal standard. Alkamides **5**, **8**, **9**, and **15** and unknowns **C1**–**C3** (all with similar UV spectra) were also determined at UV260 nm with respect to the internal standard, using a relative-response factor derived from reference standard alkamide **8**/**9** to correct for absorbance differences between these metabolites and the internal standard. The relative-response factors of alkamide **2** and alkamides **8**/**9** were calculated at A260 nm. Amounts of authentic alkamide **2** or alkamides **8**/**9** varying between 0.625 and 3.125 μg along with 2.5 μg internal standard were injected to give an average relative-response factor of 0.0669 (R2 = 0.99) for amide 2 and 0.0932 (R2 = 0.99) for amide **8**/**9** under A260 nm. Because reference standards were not available to calculate relative-response factors for each compound with respect to the internal standard, and because several of the peaks represent as yet unidentified metabolites, the values presented for the comparison of profiles herein are relative concentrations rather than absolute values and thus are presented without units of concentration.

Statistical analysis

Metabolite concentrations from three plants per accession were averaged and organized into a 40 (accessions) × 43 (relative concentration) matrix. Because standard deviations among replicates increased with mean metabolite values, the average concentrations of more abundant (with UV absorbance) metabolites were less precisely measured than were those detected at lower levels (see **Fig. 2**). The least precisely measured lipophilic constituents have a standard deviation >1000× larger than those most precisely measured. Traditional methods to summarize patterns in concentration matrices, for example, PCA or clustering using Euclidian distance, ignore such differences in precision. The statistical methods used here account for this difference, by computing a matrix based on Canberra distances for all pairs of accessions. Distances among accessions are illustrated by generating a hierarchical cluster tree (or dendrogram) based on average linkage.

The matrix of metabolite concentrations was decomposed into contributions from unique profiles by using the model

$$Y_{ij} = \alpha_i^{(1)}\beta_j^{(1)} + \alpha_i^{(2)}\beta_j^{(2)} + \alpha_i^{(3)}\beta_j^{(3)} + \mathrm{K} + e_{ij} \quad (1),$$

where Y_{ij} is the observed relative concentration of component j in accession i, $\beta^{(k)}$ is the vector representing the k'th metabolite profile, $\alpha^{(k)}$ is the vector representing the abundance of the k'th metabolite profile in each accession, and e_{ij} is the random deviation between the observed concentration and the summed contributions of k metabolite profiles. If all observations are assumed to have the same precision, the unknown profiles, $\beta^{(k)}$, and their abundances, $\alpha^{(k)}$, can be estimated by PCA without centering or standardization. This is equivalent to a singular value decomposition of the matrix Y, which can be computed by "crisscross regression" [3]. For one profile, the crisscross regression algorithm starts with an

initial guess for $\alpha^{(1)}$. The unknown $\beta^{(1)}$ values are estimated by linear regression of columns of Y on $X = \alpha^{(1)}$. The estimated $\beta^{(1)}$ values are used to update the estimate of $\alpha^{(1)}$ by linear regression of columns of Y on $X = \beta^{(1)}$. These alternating regressions are repeated until the estimates converge.

In our case, however, the precision of an observation is related to the mean, i.e.,

$$Var\ e_{ij} = m_{ij}\,\sigma^2, \qquad (2),$$

where

$$m_{ij} = \left(\alpha_i^{(1)}\beta_j^{(1)} + \alpha_i^{(2)}\beta_j^{(2)} + \alpha_i^{(3)}\beta_j^{(3)} + \mathrm{K}\right)^2 \qquad (3).$$

When the variance multipliers, m_{ij}, are known, the optimal estimator of a multiple regression slope is the weighted least-squares estimator with a weight proportional to the inverse of the variance. The unknowns $\alpha^{(k)}$ and $\beta^{(k)}$ can be estimated by combining crisscross regression with iteratively reweighted least squares. The weighted principal components analysis algorithm to estimate $\alpha^{(k)}$ and $\beta^{(k)}$ for a total of K profiles is:

- Assemble the K vectors of profiles into a matrix β with K rows and J columns.
- Assemble the K vectors of abundances into a matrix α with I rows and K columns.
- Use starting values for α and β to calculate a starting mean matrix, $m = \alpha\beta$.
- Compute the weight matrix with elements $w_{ij} = (1 / m_{ij})^2$.
- Given the current profiles, β, estimate abundances, α, by weighted multiple regression of columns of Y on β using the matching column of w as weights.
- Given the updated matrix of abundances, α, estimate profiles, β, by weighted multiple regression of columns of Y on α using the matching column of w as weights.

- Recompute the mean and weight matrices by using the updated matrices of profiles and abundances.
- Repeat the last three steps until the profile and abundance matrices converge.

The solutions are illustrated by plotting the *K* profiles and corresponding abundances.

Accessions were clustered by computing a distance measure between their chemical compositions. Unequal precision can be incorporated into a distance measure by weighting each pairwise contribution. For example, the weighted version of Manhattan Distance between accessions *a* and *b* is

$$MD_{ab} = \sum_j w_{abj} | Y_{aj} - Y_{bj} | \quad (4),$$

where Y_{aj} and Y_{bj} are the concentrations of component *j* in accessions *a* and *b* and w_{abj} is the appropriate weight for that contribution to the overall distance. When the measurement standard deviation is proportional to the mean value, the optimal weight is the reciprocal of the mean, $w_{abj} = (Y_{aj} + Y_{bj}) / 2$. The resulting distance measure is proportional to the distance measure known as the Canberra distance or Lance–Williams distance [4]:

$$CD_{ab} = \frac{1}{J} \sum_{j=1}^{J} \frac{| Y_{aj} - Y_{bj} |}{Y_{aj} + Y_{bj}} \quad (5).$$

References

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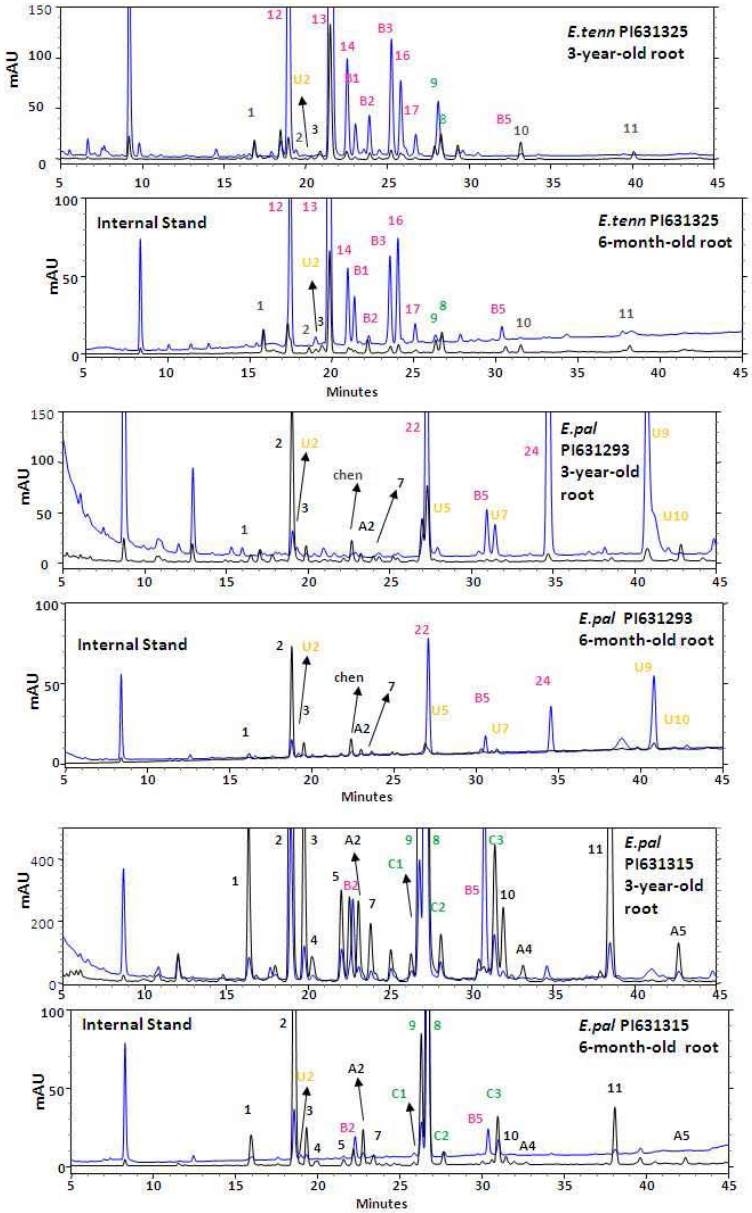


Fig. 1S HPLC chromatograms representing lipophilic metabolite profiles in roots from 6-month-old and 3-year-old plants of 3 accessions of *Echinacea*. Blue: HPLC chromatograms at UV length of 210 nm; Black: HPLC chromatograms at UV length of 260 nm.

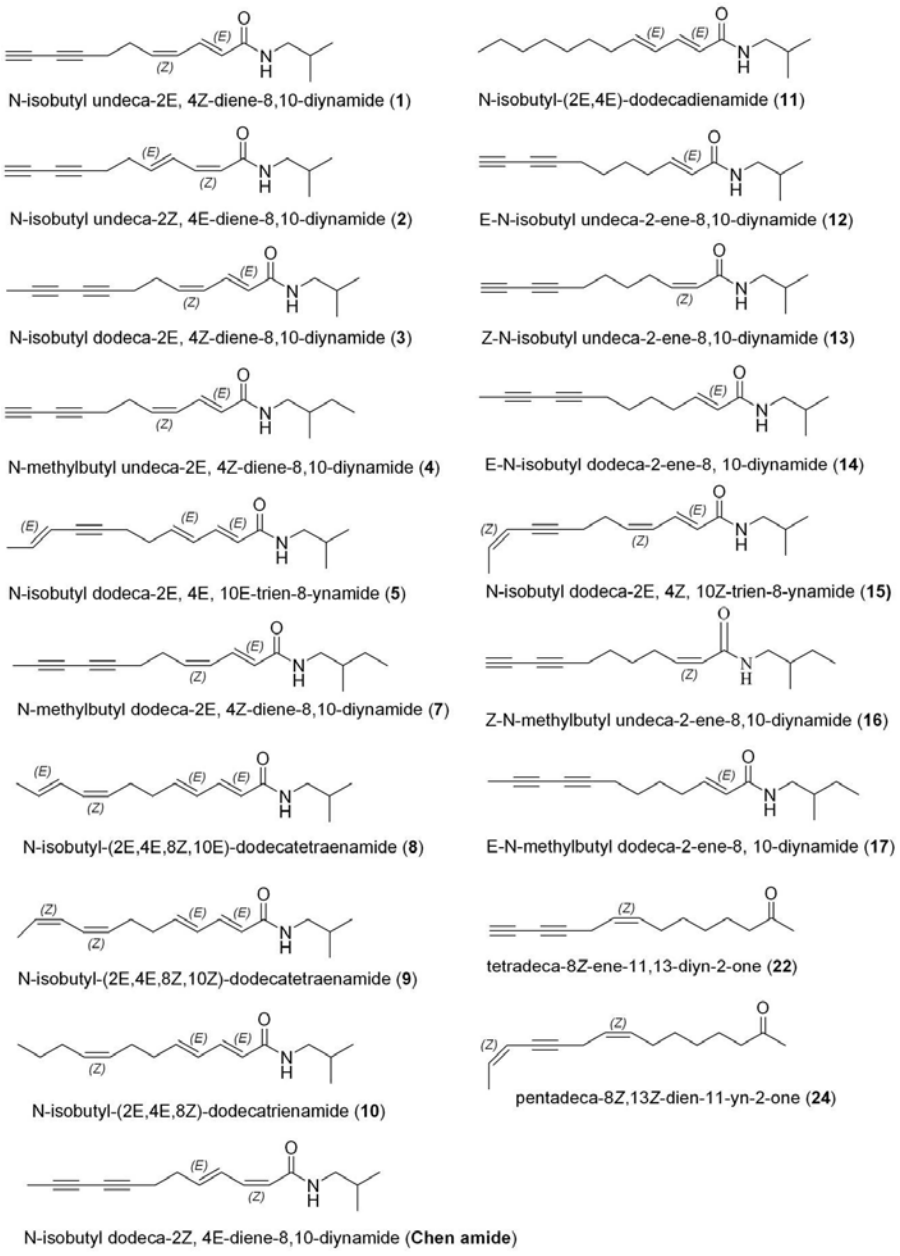
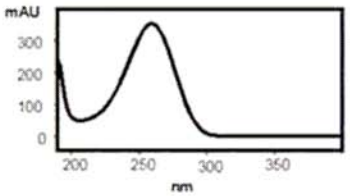


Fig. 2S Structures of identified lipophilic metabolites in *Echinacea* species (compound numbering as denoted by Bauer et al. [5]).

Fig. 3S HPLC chromatograms representing lipophilic metabolite profiles in roots from 6-month-old plants of 40 accessions of *Echinacea*. Three plants were analyzed independently for each accession with similar results. Blue: HPLC chromatograms at UV length of 210 nm; Black: HPLC chromatograms at UV length of 260 nm.

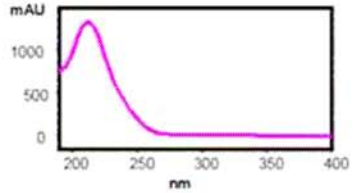
Table 1S Lipophilic metabolites found in roots of *Echinacea* species

Peak NO	Retention Time (min)	Compound
1	12.2	unknown A1
2	13.65	unknown 1
3	17	amide 1
4	18.38	amide 12
5	19.65	amide 2
6	20	unknown 2
7	20.32	amide 3
8	20.88	amide 13
9	21.03	amide 4
10	22	amide 14
11	23	unknown B1
12	22.65	amide 5
13	23.28	Chen amide
14	23.3	unknown B2
15	23.92	unknown A2
16	24.5	amide 7
17	24.66	unknown B3
18	24.83	unknown A3
19	25.14	amide 16
20	25.33	unknown 3
21	25.75	amide 15
22	26.11	unknown 4
23	26.17	amide 17
24	26.5	unknown B4
25	26.9	unknown C1
26	27.38	amide 9
27	27.75	amide 8
28	28.1	ketone 22
29	28.52	unknown 5
30	28.75	unknown C2
31	31.45	unknown B5
32	31.9	unknown 6
33	32.08	unknown C3
34	32.32	unknown 7
35	32.55	amide 10
36	33.83	unknown A4
37	35.36	unknown B6
38	35.58	ketone 24
39	39.37	amide 11
40	41	unknown 8
41	41.92	unknown 9
42	43.68	unknown A5
43	43.94	unknown 10



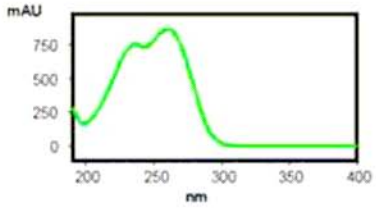
UV_{max}: 260nm

Amide 1, 2, 3, 4, 7, 10, 11, chen amide and unknown A



UV_{max} : 210nm

Amide 12, 13, 14, 16, 17 and unknown B



UV_{max}: 235nm, 260nm

Amide 5, 8, 9, 15 and unknown C

Note: A mixture of alkamides **8/9** (97% purity) was purchased (Phytolab). Alkamides **2**, **8**, **10**, **11**, **12**, **13**, and **14**, Chen alkamide, and ketone **22** were synthesized in-house. Analysis

of the ^{1}H-NMR and mass spectra of these synthesized compounds reflected purity >90%. In the absence of standards for selected compounds, alkamides **1**, **3**, **4**, **5**, **7**, **15**, **16**, and **17** and ketone **24** were identified by HPLC fractionation coupled with GC–MS analysis.
Metabolites were grouped according to their UV spectra. Gray: maximum UV absorption at 260 nm; pink: maximum UV absorption at 210 nm; green: maximum UV absorptions at 235 nm and 260 nm; yellow: atypical UV spectra.

Table 2S Relative abundance of each metabolite in roots from 6-month-old plants of 40 accessions of *Echinacea*

	Ang267	AngAng272	AngAng285	AngAng318	AngStr266	AngStr320	Atr255	Atr260	Atr262	Atr299	Hyb294	Hyb306	Lae310	Lae312	Lae314	Lae316	Pal315	Pal275	Pal290	Pal293
Unknown A1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Unknown 1	0.000	0.000	0.000	0.168	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.049	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Amide 1	0.005	0.014	0.021	0.000	0.024	0.003	0.197	0.106	0.046	0.051	0.010	0.003	0.023	0.034	0.117	0.038	0.139	0.028	0.007	0.012
	0.001	0.001	0.003	0.000	0.005	0.001	0.008	0.033	0.007	0.004	0.003	0.002	0.000	0.005	0.011	0.005	0.013	0.004	0.001	0.002
Amide 12	0.069	0.067	0.212	0.219	0.267	0.000	0.312	0.355	0.161	0.286	0.000	0.000	0.090	0.126	0.120	0.063	0.000	0.084	0.000	0.000
	0.003	0.011	0.013	0.008	0.046	0.000	0.066	0.049	0.016	0.046	0.000	0.000	0.002	0.024	0.007	0.005	0.000	0.006	0.000	0.000
Amide 2	0.023	0.041	0.054	0.023	0.058	0.095	0.006	0.117	0.001	0.001	0.445	0.058	0.118	0.236	0.064	0.116	0.376	0.023	0.126	0.066
	0.006	0.003	0.013	0.002	0.008	0.010	0.001	0.010	0.000	0.000	0.090	0.007	0.018	0.028	0.009	0.012	0.041	0.002	0.007	0.006
Unknown 2	0.000	0.000	0.020	0.030	0.000	0.038	0.025	0.012	0.010	0.012	0.015	0.006	0.012	0.033	0.009	0.009	0.005	0.008	0.026	0.008
	0.000	0.000	0.001	0.002	0.000	0.002	0.001	0.003	0.001	0.001	0.003	0.001	0.001	0.007	0.002	0.003	0.001	0.001	0.000	0.000
Amide 3	0.025	0.127	0.121	0.014	0.063	0.011	0.090	0.121	0.085	0.051	0.011	0.007	0.352	0.273	0.621	0.265	0.050	0.025	0.019	0.006
	0.004	0.019	0.016	0.001	0.015	0.003	0.013	0.008	0.010	0.013	0.001	0.002	0.018	0.028	0.085	0.027	0.013	0.002	0.002	0.002
Amide 13	0.099	0.122	0.214	0.357	0.242	0.000	0.000	0.039	0.002	0.006	0.000	0.000	0.094	0.103	0.003	0.013	0.000	0.084	0.000	0.000
	0.006	0.016	0.025	0.017	0.054	0.000	0.000	0.010	0.000	0.001	0.000	0.000	0.018	0.021	0.002	0.002	0.000	0.007	0.000	0.000
Amide 4	0.000	0.000	0.000	0.000	0.000	0.000	0.034	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.019	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000
Amide 14	0.027	0.087	0.135	0.099	0.061	0.000	0.035	0.040	0.065	0.048	0.000	0.000	0.056	0.052	0.064	0.026	0.000	0.013	0.000	0.000
	0.006	0.009	0.037	0.007	0.014	0.000	0.011	0.008	0.007	0.016	0.000	0.000	0.006	0.010	0.016	0.009	0.000	0.002	0.000	0.000
Unknown B1	0.005	0.000	0.000	0.000	0.033	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Amide 5	0.304	0.239	0.196	0.065	0.192	0.000	0.576	0.328	0.296	0.191	0.015	0.006	0.013	0.030	0.029	0.020	0.000	0.101	0.004	0.010
	0.063	0.038	0.023	0.009	0.028	0.000	0.024	0.014	0.025	0.017	0.003	0.001	0.004	0.004	0.004	0.004	0.000	0.016	0.000	0.001
Chen amide	0.000	0.023	0.017	0.042	0.007	0.087	0.000	0.000	0.000	0.000	0.082	0.019	0.095	0.084	0.033	0.057	0.000	0.000	0.019	0.017
	0.000	0.002	0.003	0.004	0.002	0.014	0.000	0.000	0.000	0.000	0.024	0.004	0.020	0.017	0.002	0.008	0.000	0.000	0.002	0.006
Unknown B2	0.055	0.000	0.000	0.000	0.069	0.000	0.081	0.023	0.038	0.071	0.000	0.000	0.000	0.000	0.000	0.000	0.056	0.131	0.000	0.000
	0.003	0.000	0.000	0.000	0.019	0.000	0.025	0.009	0.006	0.013	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.018	0.000	0.000
Unknown A2	0.000	0.000	0.000	0.000	0.000	0.008	0.000	0.000	0.000	0.000	0.025	0.003	0.004	0.007	0.003	0.006	0.028	0.000	0.008	0.006
	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.005	0.001	0.001	0.001	0.002	0.002	0.002	0.000	0.002	0.001
Amide 7	0.010	0.019	0.000	0.000	0.012	0.003	0.032	0.016	0.000	0.000	0.000	0.000	0.051	0.041	0.073	0.062	0.014	0.000	0.012	0.006
	0.001	0.002	0.000	0.000	0.001	0.001	0.001	0.006	0.000	0.000	0.000	0.000	0.006	0.008	0.025	0.008	0.001	0.000	0.002	0.002
Unknown B3	0.000	0.000	0.000	0.103	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.011	0.000	0.000
	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000
Unknown A3	0.000	0.000	0.000	0.000	0.000	0.000	0.010	0.000	0.000	0.000	0.000	0.000	0.007	0.005	0.010	0.009	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.003	0.002	0.000	0.000	0.000	0.000
Amide 16	0.000	0.027	0.028	0.033	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.007	0.000	0.000
	0.000	0.006	0.002	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000
Unknown 3	0.016	0.008	0.000	0.000	0.045	0.005	0.013	0.004	0.001	0.017	0.000	0.000	0.020	0.007	0.018	0.007	0.000	0.000	0.000	0.000
	0.003	0.001	0.000	0.000	0.015	0.001	0.005	0.001	0.001	0.002	0.000	0.000	0.002	0.001	0.009	0.004	0.000	0.000	0.000	0.000
Amide 15	0.043	0.034	0.000	0.016	0.011	0.019	0.000	0.000	0.000	0.000	0.157	0.028	0.000	0.000	0.000	0.000	0.000	0.032	0.000	0.000
	0.013	0.009	0.000	0.002	0.004	0.003	0.000	0.000	0.000	0.000	0.004	0.005	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.000
Unknown 4	0.000	0.000	0.000	0.000	0.000	0.007	0.000	0.000	0.000	0.000	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Amide 17	0.013	0.025	0.044	0.011	0.022	0.000	0.008	0.006	0.009	0.007	0.000	0.000	0.013	0.009	0.005	0.005	0.000	0.003	0.000	0.000
	0.004	0.007	0.003	0.001	0.009	0.000	0.001	0.003	0.001	0.003	0.000	0.000	0.002	0.001	0.002	0.000	0.000	0.001	0.000	0.000

Unknown B4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Unknown C1	0.071	0.030	0.037	0.000	0.041	0.000	0.238	0.061	0.053	0.036	0.000	0.000	0.000	0.000	0.000	0.000	0.011	0.017	0.000	0.000
	0.006	0.004	0.002	0.000	0.010	0.000	0.022	0.016	0.006	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.001	0.000	0.000
Amide 9	0.188	0.335	0.259	1.683	0.215	0.000	1.136	0.603	0.667	0.431	0.000	0.000	0.010	0.018	0.016	0.011	0.225	0.265	0.000	0.000
	0.038	0.079	0.040	0.143	0.051	0.000	0.123	0.122	0.068	0.057	0.000	0.000	0.002	0.004	0.002	0.002	0.039	0.041	0.000	0.000
Amide 8	0.515	0.994	2.211	1.413	1.924	0.013	1.708	1.751	0.701	0.471	0.000	0.000	0.047	0.046	0.039	0.059	2.051	2.432	0.000	0.000
	0.019	0.135	0.406	0.085	0.375	0.002	0.074	0.243	0.040	0.066	0.000	0.000	0.003	0.005	0.009	0.001	0.192	0.317	0.000	0.000
Ketone 22	0.000	0.000	0.000	0.000	0.000	0.103	0.000	0.000	0.000	0.000	0.131	0.051	0.058	0.062	0.027	0.016	0.000	0.000	0.136	0.242
	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.039	0.011	0.005	0.007	0.007	0.004	0.000	0.000	0.007	0.005
Unknown 5	0.000	0.000	0.000	0.000	0.000	0.005	0.000	0.000	0.000	0.000	0.021	0.014	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.006
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001
Unknown C2	0.009	0.014	0.016	0.108	0.006	0.000	0.055	0.030	0.029	0.022	0.000	0.000	0.000	0.000	0.000	0.000	0.017	0.009	0.000	0.000
	0.003	0.002	0.003	0.012	0.001	0.000	0.005	0.009	0.004	0.008	0.000	0.000	0.000	0.000	0.000	0.000	0.006	0.002	0.000	0.000
Unknown B5	0.066	0.097	0.234	0.276	0.402	0.000	0.172	0.132	0.090	0.109	0.000	0.000	0.000	0.000	0.000	0.000	0.069	0.198	0.044	0.028
	0.010	0.007	0.024	0.019	0.090	0.000	0.012	0.023	0.002	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.006	0.008	0.010
Unknown 6	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Unknown C3	0.013	0.014	0.061	0.037	0.063	0.000	0.079	0.032	0.012	0.012	0.000	0.000	0.000	0.000	0.000	0.000	0.051	0.044	0.000	0.000
	0.004	0.002	0.004	0.005	0.009	0.000	0.007	0.004	0.001	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.008	0.005	0.000	0.000
Unknown 7	0.000	0.000	0.000	0.000	0.000	0.022	0.000	0.000	0.000	0.000	0.017	0.008	0.039	0.017	0.019	0.009	0.000	0.000	0.022	0.012
	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.005	0.002	0.002	0.003	0.002	0.001	0.000	0.000	0.002	0.002
Amide 10	0.087	0.152	0.168	0.105	0.167	0.000	0.121	0.111	0.039	0.063	0.000	0.000	0.000	0.000	0.000	0.000	0.040	0.101	0.000	0.000
	0.018	0.021	0.026	0.007	0.028	0.000	0.004	0.024	0.003	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.007	0.016	0.000	0.000
Unknown A4	0.000	0.010	0.017	0.012	0.008	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.007	0.011	0.000	0.000
	0.000	0.002	0.001	0.002	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.001	0.000	0.000
Unknown B6	0.000	0.017	0.035	0.044	0.037	0.000	0.021	0.006	0.008	0.006	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.001	0.003	0.002	0.010	0.000	0.001	0.002	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ketone 24	0.000	0.000	0.000	0.000	0.000	0.313	0.000	0.000	0.000	0.000	1.113	0.577	0.000	0.000	0.000	0.000	0.000	0.000	0.106	0.226
	0.000	0.000	0.000	0.000	0.000	0.017	0.000	0.000	0.000	0.000	0.217	0.043	0.000	0.000	0.000	0.000	0.000	0.000	0.007	0.024
Amide 11	0.088	0.162	0.442	0.269	0.135	0.000	0.062	0.074	0.040	0.055	0.000	0.000	0.006	0.008	0.005	0.010	0.154	0.366	0.003	0.000
	0.006	0.026	0.052	0.019	0.036	0.000	0.003	0.018	0.004	0.006	0.000	0.000	0.001	0.001	0.002	0.002	0.028	0.032	0.000	0.000
Unknown 8	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Unknown 9	0.000	0.000	0.000	0.000	0.000	0.038	0.000	0.000	0.000	0.000	0.083	0.026	0.000	0.000	0.000	0.000	0.000	0.000	0.096	0.123
	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.026	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.007	0.018
Unknown A5	0.000	0.000	0.022	0.009	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.009	0.010	0.000	0.000
	0.000	0.000	0.001	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000
Unknown 10	0.000	0.000	0.000	0.000	0.000	0.017	0.000	0.000	0.000	0.000	0.055	0.044	0.000	0.000	0.000	0.000	0.000	0.000	0.013	0.013
	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.013	0.009	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.001

	Pal296	ParaNeg263	ParaNeg264	ParaNeg265	ParaPara292	ParaPara301	ParaPara321	Pur307	Pur313	Pur504	Sang257	Sang258	Sang878	Simu249	Simu304	Simu308	Tenn250	Tenn324	Tenn325	Tenn326
Unknown A1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.008	0.011	0.015	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Unknown 1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Amide 1	0.007	0.002	0.001	0.003	0.007	0.004	0.006	0.332	0.040	0.474	0.061	0.147	0.269	0.008	0.004	0.006	0.013	0.005	0.027	0.003
	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.042	0.004	0.023	0.007	0.019	0.043	0.001	0.001	0.000	0.002	0.001	0.004	0.001
Amide 12	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.154	0.416	0.285	0.011	0.000	0.000	0.269	0.580	0.225	0.157
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.013	0.033	0.049	0.001	0.000	0.000	0.027	0.007	0.035	0.026
Amide 2	0.194	0.053	0.028	0.064	0.293	0.145	0.249	0.727	0.500	0.228	0.009	0.033	0.088	0.129	0.114	0.106	0.012	0.014	0.007	0.009
	0.014	0.003	0.003	0.006	0.045	0.003	0.045	0.029	0.057	0.025	0.003	0.002	0.002	0.010	0.011	0.008	0.005	0.002	0.001	0.002
Unknown 2	0.015	0.012	0.008	0.010	0.014	0.000	0.000	0.024	0.016	0.020	0.006	0.010	0.011	0.000	0.000	0.000	0.016	0.013	0.012	0.014
	0.002	0.001	0.001	0.000	0.001	0.000	0.000	0.002	0.000	0.003	0.000	0.001	0.002	0.000	0.000	0.000	0.001	0.002	0.001	0.002
Amide 3	0.015	0.017	0.008	0.003	0.015	0.020	0.019	0.115	0.655	1.239	0.184	0.332	0.292	0.054	0.013	0.058	0.012	0.018	0.013	0.016
	0.002	0.001	0.002	0.000	0.004	0.000	0.003	0.009	0.009	0.118	0.023	0.015	0.067	0.010	0.002	0.004	0.001	0.001	0.002	0.005
Amide 13	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.040	0.150	0.236	0.008	0.000	0.000	0.598	1.080	1.195	1.103
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.006	0.018	0.020	0.001	0.000	0.000	0.021	0.020	0.106	0.033
Amide 4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.014	0.077	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Amide 14	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.206	0.441	0.318	0.002	0.000	0.000	0.062	0.148	0.070	0.109
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.036	0.022	0.025	0.000	0.000	0.000	0.006	0.014	0.006	0.001
Unknown B1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.016	0.070	0.043	0.030
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.012	0.005	0.003
Amide 5	0.004	0.003	0.004	0.002	0.000	0.000	0.000	0.221	0.058	0.228	0.022	0.052	0.054	0.016	0.000	0.014	0.000	0.000	0.000	0.000
	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.038	0.006	0.009	0.008	0.005	0.007	0.001	0.000	0.001	0.000	0.000	0.000	0.000
Chen amide	0.074	0.077	0.021	0.037	0.119	0.106	0.125	0.777	0.996	0.078	0.009	0.045	0.061	0.075	0.046	0.037	0.000	0.000	0.000	0.000
	0.006	0.006	0.003	0.003	0.016	0.013	0.027	0.043	0.062	0.004	0.004	0.011	0.004	0.014	0.007	0.001	0.000	0.000	0.000	0.000
Unknown B2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.014	0.022	0.010	0.012
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.002	0.002	0.002
Unknown A2	0.011	0.003	0.002	0.005	0.022	0.016	0.013	0.126	0.034	0.017	0.000	0.000	0.000	0.007	0.011	0.005	0.000	0.000	0.000	0.000
	0.000	0.000	0.001	0.000	0.004	0.004	0.003	0.025	0.006	0.002	0.000	0.000	0.000	0.002	0.001	0.000	0.000	0.000	0.000	0.000
Amide 7	0.008	0.000	0.000	0.000	0.004	0.011	0.005	0.236	0.225	0.207	0.021	0.059	0.046	0.011	0.005	0.020	0.000	0.000	0.000	0.000
	0.001	0.000	0.000	0.000	0.001	0.001	0.000	0.025	0.004	0.011	0.002	0.004	0.010	0.003	0.001	0.001	0.000	0.000	0.000	0.000
Unknown B3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.012	0.048	0.028	0.000	0.000	0.000	0.063	0.057	0.088	0.120
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.007	0.003	0.000	0.000	0.000	0.007	0.004	0.006	0.024
Unknown A3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.042	0.053	0.034	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.002	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Amide 16	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.007	0.021	0.018	0.000	0.000	0.000	0.031	0.085	0.099	0.076
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.006	0.003	0.000	0.000	0.000	0.005	0.001	0.007	0.010
Unknown 3	0.000	0.002	0.019	0.002	0.004	0.002	0.002	0.031	0.006	0.018	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.001	0.001	0.000	0.001	0.001	0.001	0.002	0.001	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Amide 15	0.000	0.025	0.011	0.013	0.066	0.074	0.090	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.002	0.002	0.001	0.007	0.006	0.009	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Unknown 4	0.000	0.013	0.014	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.002	0.003	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Amide 17	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.042	0.118	0.048	0.000	0.000	0.000	0.011	0.048	0.014	0.025

	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.006	0.037	0.008	0.000	0.000	0.000	0.005	0.004	0.005	0.009
Unknown B4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.011	0.029	0.006	0.000	0.000	0.000	0.002	0.006	0.000	0.003
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.002	0.000	0.000	0.000	0.000	0.001	0.000	0.001
Unknown C1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.130	0.023	0.052	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.006	0.004	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Amide 9	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.459	0.024	0.057	0.468	0.872	0.768	0.031	0.000	0.000	0.054	0.208	0.024	0.007
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.029	0.002	0.004	0.030	0.119	0.205	0.005	0.000	0.000	0.005	0.012	0.002	0.001
Amide 8	0.000	0.000	0.000	0.000	0.019	0.000	0.030	0.296	0.259	0.433	1.831	3.269	2.603	0.057	0.017	0.019	0.063	0.227	0.039	0.068
	0.000	0.000	0.000	0.000	0.005	0.000	0.007	0.024	0.022	0.080	0.159	0.246	0.357	0.003	0.003	0.003	0.004	0.019	0.005	0.020
Ketone 22	0.154	0.063	0.088	0.110	0.147	0.073	0.120	0.000	0.000	0.000	0.000	0.000	0.000	0.074	0.099	0.061	0.000	0.000	0.000	0.000
	0.005	0.007	0.018	0.005	0.011	0.012	0.018	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.004	0.006	0.000	0.000	0.000	0.000
Unknown 5	0.006	0.003	0.005	0.005	0.014	0.007	0.015	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.004	0.002	0.000	0.000	0.000	0.000
	0.001	0.000	0.001	0.001	0.002	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Unknown C2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Unknown B5	0.093	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.030	0.099	0.207	0.124	0.086	0.009	0.007	0.000	0.000	0.013	0.013
	0.014	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.015	0.012	0.015	0.006	0.001	0.001	0.000	0.000	0.003	0.003
Unknown 6	0.000	0.003	0.006	0.011	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Unknown C3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.037	0.060	0.063	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.017	0.016	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Unknown 7	0.022	0.026	0.024	0.011	0.050	0.029	0.031	0.000	0.000	0.000	0.000	0.000	0.000	0.010	0.018	0.011	0.000	0.000	0.000	0.000
	0.003	0.003	0.005	0.000	0.005	0.003	0.007	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.002	0.001	0.000	0.000	0.000	0.000
Amide 10	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.055	0.014	0.048	0.048	0.077	0.082	0.000	0.000	0.000	0.043	0.039	0.010	0.030
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.001	0.003	0.001	0.009	0.011	0.000	0.000	0.000	0.006	0.004	0.001	0.012
Unknown A4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Unknown B6	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.018	0.025	0.021	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.002	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ketone 24	0.208	0.262	0.468	0.398	0.527	0.361	0.659	0.000	0.000	0.000	0.000	0.000	0.000	0.055	0.092	0.107	0.000	0.000	0.000	0.000
	0.031	0.032	0.035	0.006	0.053	0.016	0.022	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.003	0.012	0.000	0.000	0.000	0.000
Amide 11	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.032	0.010	0.044	0.023	0.056	0.068	0.010	0.000	0.000	0.028	0.036	0.011	0.015
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.007	0.002	0.004	0.003	0.008	0.006	0.002	0.000	0.000	0.005	0.003	0.002	0.004
Unknown 8	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.017	0.023	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Unknown 9	0.202	0.014	0.050	0.105	0.036	0.039	0.029	0.000	0.000	0.000	0.000	0.000	0.000	0.026	0.042	0.046	0.000	0.000	0.000	0.000
	0.011	0.001	0.003	0.004	0.004	0.006	0.006	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.002	0.004	0.000	0.000	0.000	0.000
Unknown A5	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Unknown 10	0.015	0.024	0.027	0.029	0.038	0.017	0.027	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.001	0.002	0.004	0.004	0.006	0.003	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Note: Results are the mean of 3 independently analyzed plants; standard deviation is shown below each mean.