

Table S1. The mean values (scopoletin and scopolin concentrations) and standard deviations (\pm SD) that were used in making heat maps shown in Figure 2.

Accession	Scopoletin concentration [μ M]				Scopolin concentration [μ M]			
	roots, H-	roots, H+	leaves, H-	leaves, H+	roots, H-	roots, H+	leaves, H-	leaves, H+
An-1	4.91 \pm 4.12	15.19 \pm 11.34	0.10 \pm 0.12	0.45 \pm 0.24	14.81 \pm 4.05	0.13 \pm 0.12	0.68 \pm 0.41	0.05 \pm 0.08
Bay-0	41.93 \pm 6.58	151.90 \pm 30.12	0.29 \pm 0.18	1.99 \pm 1.46	38.95 \pm 10.69	07.15 \pm 6.36	3.81 \pm 1.22	0.88 \pm 1.53
Br-0	35.01 \pm 9.48	139.27 \pm 49.38	0.31 \pm 0.09	2.61 \pm 0.27	67.26 \pm 23.82	1.22 \pm 0.08	1.65 \pm 0.08	0
C24	4.92 \pm 2.67	16.63 \pm 10.42	0.20 \pm 0.11	0.83 \pm 0.55	41.36 \pm 24.8	0.43 \pm 0.19	0.85 \pm 0.59	0
Can-0	3.14 \pm 1.89	64.03 \pm 84.91	0.14 \pm 0.14	0.37 \pm 0.12	34.63 \pm 4.85	0.56 \pm 0.05	2.23 \pm 1.24	0.19 \pm 0.33
Col-0	11.79 \pm 3.16	29.60 \pm 11.41	0.31 \pm 0.41	1.16 \pm 0.99	11.47 \pm 3.41	0.46 \pm 0.07	1.48 \pm 0.67	0
Cvi-1	4.58 \pm 0.62	11.54 \pm 7.57	0.19 \pm 0.10	0.61 \pm 0.27	35.41 \pm 32.83	0.35 \pm 0.16	2.15 \pm 0.8	0
Eil-0	8.03 \pm 4.90	21.55 \pm 14.72	0.15 \pm 0.03	0.53 \pm 0.23	28.24 \pm 11.10	1.12 \pm 0.2	2.19 \pm 1.16	0.02 \pm 0
Eri-0	12.86 \pm 3.96	23.84 \pm 13.33	0.13 \pm 0.09	0.68 \pm 0.48	20.55 \pm 8.45	2.04 \pm 0.3	2.24 \pm 0.93	0.03 \pm 0.04
Est-1	14.85 \pm 1.63	36.79 \pm 2.44	0.42 \pm 0.19	2.01 \pm 0.86	32.22 \pm 12.66	0.44 \pm 0.2	6.48 \pm 3.7	0.07 \pm 0.09
Fei-0	12.82 \pm 8.73	52.02 \pm 15.32	0.09 \pm 0.06	0.73 \pm 0.37	62.36 \pm 28.64	0.52 \pm 0.08	2.77 \pm 1.53	0.08 \pm 0.13
Fuk-1	13.06 \pm 7.87	44.36 \pm 47.37	0.13 \pm 0.01	0.62 \pm 0.11	29.23 \pm 27.52	8.09 \pm 7.02	1.58 \pm 0.62	0.05 \pm 0.09
Ga-0	3.40 \pm 1.11	19.67 \pm 12.65	0.03 \pm 0.01	0.55 \pm 0.16	53.08 \pm 7.05	1.29 \pm 0.25	3.03 \pm 0.58	0.12 \pm 0.25
Hog	7.47 \pm 7.02	20.31 \pm 20.17	0.10 \pm 0.06	0.34 \pm 0.12	16.9 \pm 14.41	0.85 \pm 0.52	1.03 \pm 0.46	0
Kas-2	4.95 \pm 0.33	22.71 \pm 7.70	0.04 \pm 0.01	0.39 \pm 0.21	21.39 \pm 17.39	0.59 \pm 0.26	1.54 \pm 0.63	0.24 \pm 0.41
Kondara	42.79 \pm 9.84	81.30 \pm 25.39	0.26 \pm 0.27	1.05 \pm 0.29	25.10 \pm 16.58	0.86 \pm 0.71	0.80 \pm 0.14	0.04 \pm 0.08
Kyo-0	5.20 \pm 1.63	26.87 \pm 18.45	0.04 \pm 0.04	0.82 \pm 0.53	33.97 \pm 12.23	0.77 \pm 0.26	3.50 \pm 2.50	0
Leb 3/4	17.93 \pm 5.89	34.91 \pm 19.59	0.19 \pm 0.11	0.72 \pm 0.36	41.77 \pm 27.88	0.84 \pm 0.19	2.26 \pm 1.41	0
Ler-1	3.88 \pm 1.52	8.89 \pm 2.94	0.04 \pm 0.07	0.27 \pm 0.05	2.94 \pm 0.66	0.23 \pm 0.07	0.69 \pm 0.07	0.16 \pm 0.27
No-0	2.61 \pm 1.17	8.35 \pm 8.20	0.19 \pm 0.14	1.10 \pm 0.92	10.26 \pm 6.89	1.09 \pm 0.16	3.41 \pm 1.92	0.06 \pm 0.11
Ri-0	11.42 \pm 4.05	44.55 \pm 21.08	0.13 \pm 0.06	0.48 \pm 0.49	41.47 \pm 25.01	5.15 \pm 0.93	2.06 \pm 1.03	0
Sf-2	5.12 \pm 3.51	11.29 \pm 8.85	0.05 \pm 0.03	0.22 \pm 0.14	10.67 \pm 8.42	0.42 \pm 0.15	0.99 \pm 0.29	0
Sha-1	15.46 \pm 0.67	36.68 \pm 2.00	0.15 \pm 0.11	0.73 \pm 0.56	31.31 \pm 6.11	3.16 \pm 0.89	2.32 \pm 1.99	0.15 \pm 0.26
Sorbo	15.17 \pm 4.57	26.08 \pm 16.16	0.24 \pm 0.26	1.35 \pm 0.83	9.12 \pm 6.08	0.99 \pm 0.27	5.01 \pm 3.04	0.69 \pm 0.85
Ts-5	4.75 \pm 0.38	16.47 \pm 14.26	0.08 \pm 0.07	0.92 \pm 0.55	7.89 \pm 4.64	0.64 \pm 0.13	0.92 \pm 0.61	0
Tsu-1	2.71 \pm 0.78	10.32 \pm 1.96	0.03 \pm 0.02	0.14 \pm 0.04	12.53 \pm 6.06	0.87 \pm 0.33	0.35 \pm 0.09	0.01 \pm 0.01
Van-0	4.01 \pm 3.01	8.02 \pm 11.19	0.10 \pm 0.09	0.77 \pm 0.93	7.98 \pm 6.97	0.24 \pm 0.09	2.30 \pm 1.33	0.13 \pm 0.12
Ws-0	9.68 \pm 5.92	19.16 \pm 18.60	0.16 \pm 0.12	0.54 \pm 0.12	30.49 \pm 27.29	0.58 \pm 0.15	2.58 \pm 0.36	0.26 \pm 0.24

Table S2. The mean values (umbelliferone and skimmin concentrations) and standard deviations (\pm SD) that were used in making heat maps shown in Figure 3.

Accession	Umbelliferone concentration [μ M]				Skimmin concentration [μ M]			
	roots, H-	roots, H+	leaves, H-	leaves, H+	roots, H-	roots, H+	leaves, H-	leaves, H+
An-1	0.02 \pm 0.03	0.23 \pm 0.15	0	0	3.53 \pm 2.92	0.23 \pm 0.34	0.30 \pm 0.03	0
Bay-0	0.16 \pm 0.08	1.64 \pm 0.14	0	0	7.32 \pm 1.51	5.40 \pm 2.98	0	0
Br-0	0.06 \pm 0.02	1.05 \pm 1.01	0	0	3.19 \pm 1.58	0.59 \pm 0.17	0	0
C24	0.06 \pm 0.11	0.97 \pm 0.59	0	0	15.25 \pm 9.47	3.48 \pm 4.57	0.30 \pm 0.04	0
Can-0	0	0.30 \pm 0.36	0	0	2.59 \pm 0.61	0.76 \pm 0.57	0.07 \pm 0.05	0
Col-0	0.15 \pm 0.10	1.06 \pm 0.17	0	0	8.40 \pm 5.60	0.43 \pm 0.41	0.29 \pm 0.24	0.07 \pm 0.08
Cvi-1	0	0.07 \pm 0.05	0	0	2.70 \pm 2.16	0.13 \pm 0.11	0	0
Eil-0	0	0.09 \pm 0.04	0	0	6.38 \pm 2.34	0.60 \pm 0.48	0	0
Eri-0	0.14 \pm 0.06	0.42 \pm 0.27	0	0	9.76 \pm 2.83	0.68 \pm 0.69	0.34 \pm 0.13	0
Est-1	0.07 \pm 0.09	1.09 \pm 0.67	0	0	12.27 \pm 0.26	1.64 \pm 0.55	0	0
Fei-0	0.05 \pm 0.04	0.31 \pm 0.08	0	0	3.42 \pm 2.05	0.37 \pm 0.41	0	0
Fuk-1	0.10 \pm 0.09	0.72 \pm 0.60	0	0	1.34 \pm 0.42	2.81 \pm 3.43	0.10 \pm 0.05	0
Ga-0	0	0.20 \pm 0.16	0	0	19.80 \pm 3.01	2.00 \pm 1.49	0.13 \pm 0.11	0
Hog	0	0.03 \pm 0.04	0	0	5.87 \pm 1.67	1.43 \pm 0.87	0	0
Kas-2	0	0.63 \pm 0.18	0	0	2.62 \pm 0.61	0.09 \pm 0.05	0	0
Kondara	0.02 \pm 0.04	0.50 \pm 0.38	0	0	5.11 \pm 1.26	0.36 \pm 0.28	0.19 \pm 0.10	0.01 \pm 0.02
Kyo-0	0	0.40 \pm 0.27	0	0	11.60 \pm 3.00	1.14 \pm 0.08	0	0
Leb 3/4	0.11 \pm 0.02	0.72 \pm 0.38	0	0	4.25 \pm 2.36	0.20 \pm 0.13	0	0
Ler-1	0.03 \pm 0.02	0.34 \pm 0.11	0	0	2.21 \pm 0.57	0.48 \pm 0.07	0	0
No-0	0	0.03 \pm 0.05	0	0	8.88 \pm 6.51	2.49 \pm 2.48	0	0
Ri-0	0.14 \pm 0.06	1.41 \pm 0.68	0	0	13.25 \pm 4.35	18.76 \pm 16.26	0	0
Sf-2	0	0.29 \pm 0.11	0	0	1.96 \pm 1.58	0.30 \pm 0.27	0	0
Sha-1	0.07 \pm 0.03	0.63 \pm 0.18	0	0	8.01 \pm 1.30	0.93 \pm 0.80	0	0
Sorbo	0.24 \pm 0.09	0.78 \pm 0.35	0	0	1.52 \pm 0.44	0.04 \pm 0.05	0	0
Ts-5	0	0.38 \pm 0.31	0	0	0.69 \pm 0.05	0.23 \pm 0.11	0	0
Tsu-1	0	0.29 \pm 0.07	0	0	5.82 \pm 3.00	0.51 \pm 0.35	0.04 \pm 0.06	0
Van-0	0.02 \pm 0.04	0.63 \pm 0.56	0	0	4.38 \pm 0.91	0.32 \pm 0.20	0.25 \pm 0.13	0.04 \pm 0.06
Ws-0	0.11 \pm 0.04	0.45 \pm 0.31	0	0	14.04 \pm 3.26	1.42 \pm 0.24	0.17 \pm 0.08	0.03 \pm 0.06

Table S3. The mean values (esculetin and esculin concentrations) and standard deviations (\pm SD) that were used in making heat maps shown in Figure 4.

Accession	Esculetin concentration [μ M]				Esculin concentration [μ M]			
	roots, H-	roots, H+	leaves, H-	leaves, H+	roots, H-	roots, H+	leaves, H-	leaves, H+
An-1	0	0	0.04 \pm 0.07	0	0	0	0.02 \pm 0.01	0
Bay-0	0.11 \pm 0.18	0.26 \pm 0.26	0	0	0	0	0	0
Br-0	0.07 \pm 0.12	0	0.14 \pm 0.03	0	0	0	0	0
C24	0	0	0.16 \pm 0.03	0	0	0	0.01 \pm 0.01	0
Can-0	0.01 \pm 0.02	0.29 \pm 0.51	0	0	0	0	0.09 \pm 0.15	0.15 \pm 0.13
Col-0	0	0.20 \pm 0.14	0.02 \pm 0.03	0	0	0.01 \pm 0.01	0.15 \pm 0.21	0.08 \pm 0.15
Cvi-1	0	0	0	0	0	0	0	0
Eil-0	0	0	0	0	0	0	0	0
Eri-0	0	0	0	0	0	0	0	0.07 \pm 0.12
Est-1	0	0	0	0	0	0	0.12 \pm 0.02	0
Fei-0	0	0	0	0	0	0	0	0
Fuk-1	0	0	0	0	0	0	0	0
Ga-0	0	0	0	0	0	0	0	0
Hog	0	0	0	0	0	0	0.01 \pm 0.01	0
Kas-2	0	0	0	0	0	0	0.03 \pm 0.05	0
Kondara	0	0	0	0	0	0	0	0
Kyo-0	0	0	0	0	0	0	0	0
Leb 3/4	0	0	0	0	0	0	0	0
Ler-1	0	0	0	0	0	0	0.01 \pm 0.01	0.03 \pm 0.06
No-0	0	0	0.02 \pm 0.03	0	0	0	0.02 \pm 0.04	0
Ri-0	0	0.20 \pm 0.06	0.01 \pm 0.02	0	0	0	0.04 \pm 0.07	0
Sf-2	0	0	0	0	0	0	0	0
Sha-1	0	0	0	0	0	0	0	0
Sorbo	0	0	0	0	0	0	0	0
Ts-5	0	0	0	0	0	0	0	0.01 \pm 0.02
Tsu-1	0	0.08 \pm 0.08	0	0	0	0	0	0
Van-0	0	0	0	0	0	0	0	0.06 \pm 0.08
Ws-0	0	0	0.02 \pm 0.02	0.01 \pm 0.02	0	0	0.01 \pm 0.02	0.36 \pm 0.32

Table S4. Coumarin concentrations in root samples before hydrolysis and four geographic and climatic factors used in principle component analysis (PCA). Average winter temperatures – taken from November to April; average summer temperatures – taken from May to October. Altitude and annual precipitation data are taken for the closest place where the given accession originates. Data sources [1] Temperature and precipitation (Temperature and precipitation - <https://www.climatestotravel.com/> (US: <https://www.usclimatedata.com/climate/columbia/north-carolina/united-states/usnc0145>), [2] Altitude (<https://www.freemaptools.com/elevation-finder.htm>), [3] Annual precipitation (<https://weather-and-climate.com/>).

Altitude max	AV winter min temp [°C]	AV summer max temp [°C]	AV annual precipitation [mm]	Umbelliferone	Skimmin	Scopoletin	Scopolin	Continent	Accession
100	2.5	20	850	0.231	0.014	15.186	0.006	Europe	An-1
400	-0.7	20.7	640	1.644	0.323	151.905	0.336	Europe	Bay-0
300	-0.8	21.3	493	1.05	0.036	139.274	0.057	Europe	Br-0
30	6.7	25.3	905	0.972	0.208	16.627	0.02	Europe	C24
1260	16	26.2	146	0.3	0.046	64.031	0.026	Africa	Can-0
100	3.85	27.9	1265	1.056	0.025	29.604	0.021	North America	Col-0
1200	19.8	26	97	0.067	0.008	11.538	0.016	Africa	Cvi-1
200	0.3	20.5	535	0.086	0.036	21.551	0.052	Europe	Eil-0
119	-1.5	17.8	660	0.418	0.041	23.835	0.096	Europe	Eri-1
200	-4.2	16.5	695	1.088	0.098	36.793	0.021	Europe	Est-1
140	7	22.7	1255	0.311	0.022	52.02	0.025	Europe	Fei-0
18	5.2	27.7	1540	0.721	0.475	44.36	0.379	Asia	Fuk-1
200	1.3	21.5	620	0.199	0.12	19.67	0.06	Europe	Ga-0
1887	2.3	30.5	610	0.078	0.085	20.311	0.04	Asia	Hog
1580	-1.8	27	215	0.625	0.005	22.713	0.028	Asia	Kas-2
916	2.3	30.5	610	0.499	0.022	81.3	0.04	Asia	Kondara
98	4.3	28.3	1490	0.4	0.068	26.866	0.036	Asia	Kyo-1
301	-14.6	21.2	264	0.718	0.012	34.909	0.039	Asia	Leb 3/4
614	0.3	20.5	535	0.335	0.028	8.892	0.011	Europe	Ler-1
300	0.33	20.3	665	0.089	0.149	8.353	0.051	Europe	No-0
100	2.7	19	1190	1.41	0.000	44.551	0.648	North America	Ri-0
100	6.8	25.2	620	0.288	0.018	11.291	0.02	Europe	Sf-2
3400	-4.2	25.3	233	0.627	0.056	36.684	0.148	Asia	Sha-1
646	-4.3	25.4	234	0.781	0.002	26.081	0.046	Asia	Sorbo
100	6.8	25.2	620	0.382	0.014	16.469	0.03	Europe	Ts-5
100	4.5	27.8	1535	0	0.348	2.711	0.588	Asia	Tsu-1
100	2.7	19	1190	0.628	0.019	8.022	0.011	North America	Van-0
200	-3.5	19.2	675	0.446	0.085	19.157	0.027	Europe	Ws-0