Plant-endophytes interaction influences the secondary metabolism in *Echinacea purpurea* (L.) Moench: an *in vitro* model.

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Supplementary Table 3. Spectral (UV and ESI-MS/MS) and chromatographic data (retention time, t_R) of alkamides **1-15** detected in *n*-hexane extracts of *E. purpurea* not-infected stem/leaves (SL) and roots (R), used as control, and SL and R infected by *E. purpurea* SL endophytes. MS/MS data are obtained from the fragmentation of the $[M+H]^+$ precursor ions. The peaks are related to those reported in Supplementary Figs. 2 and 3. Compound numbers are referred to alkamides listed in Table 1.

Peak	Compound	t_R (min)	M	$[M+H]^+$	$[M+Na]^+$	$[2M+H]^+$	$[2M+Na]^+$	MS/MS base peak	MS/MS ions (*m/z*)	λ_{max} (nm)	Reference
A	**1** and /or **2**	18.7	229	230	252	459	481	131	174[a], 157[b], 146, 129[c], 116, 91	260	26
B	**3** and /or **4**	22.8	243	244	266	487	509	131	216, 174[c], 157[d], 129[f], 117, 91	260	29
C	NI	23.7	263	264	286	527	549	246	222, 175, 147, 105, 93	260	NR
D	**5**	26.3	257	258	280	515	537	202[a]	185[b], 159, 157[c], 143, 131, 117, 91	260	29
	6 (only in leaves)	26.7	245	246	268	491	513	147	190[a], 173[b], 145, 131[e], 119, 105, 91	260	26
E	NI	28.3	265	266	288	531	553		–	260	NR
F	NI	30.1	245	246	268	491	513		221, 203, 190, 175, 173, 147, 119, 105, 91	260	NR
G	**7** and/or **8**	32.5	247	248	270	495	518	149	192[a], 175[b], 147[c], 142, 93, 74	260	26
H	NI	33.9	267	268	290	535	557	–	–	260	NR
I	NI	34.7	285	286	308	571	593	230	213, 195, 185, 171, 145, 131, 117, 95	250	NR
J	NI	35.4	278	279	301	557	579	204	234, 223, 203, 181, 163, 149, 135, 95	260	NR
K	**9** or **10**	36.4	261	262	284	525	545	149	234, 204, 192[c], 181, 175[d], 156, 147[f], 133, 121, 107, 93	250	28
L	**11**	36.8	249	250	272	499	521	167	194[a], 177[b], 149[c], 135, 121, 109, 95	275	26
M	NI	39.0	275	276	298	551	573	177	220, 203, 175, 135, 121, 95		NR
N	**12**	41.6	251	252	274	503	525	179[b]	196[a], 161, 137, 151[e], 119, 95,79	260	26
O	**13** or **14**	23.5	243	244	266	487	509	145	216, 202, 188[a], 171[b], 143[e], 129, 117, 105, 91	260	29
P	**15**	27.7	257	258	280	515	537	145	230, 188[c], 171[d], 143[f], 117, 105, 91	260	29

[a]Fragment $[M+H-56]^+$ originated by the loss of the isobutyl group attached to the nitrogen; [b]fragment $[M+H-73]^+$ due to the loss of the isobutyl amine; [c]fragment $[M+H-70]^+$ due to the loss of the 2-methylbutyl group attached to the nitrogen; [d]fragment $[M+H-87]^+$ corresponding to the loss of the 2-methylbutyl amine; [e]fragment $[M+H-101]^+$ due to the loss of the amide portion from an isobutylamide; [f]fragment $[M+H-115]^+$ originated by the loss of the amide portion from a 2-methylbutylamide. NR: not reported; NI: not identified. Alkamides not previously reported (peaks **C**, **E**, **F**, **H, I, J** and **M**) are ascribable to the alkamide class due to the characteristic absorbance at 260 nm and typical ESI-MS and MS/MS spectra Indeed, masses of alkamide ions are detected with ESI-MS in the positive mode, originating protonated $[M+H]^+$ and sodiated molecules $[M+Na]^+$. Protonated $[2M+H]^+$ and sodiated dimers $[2M+Na]^+$ were also commonly observed. Alkamides occurring in *E. purpurea* had structures containing ethylenic and/or acetylenic bonds and an amide portion, constituted by an isobutylamide or a 2-methylbutylamide moiety[2], displaying a high absorbance at 260 nm. These alkamides were structurally similar and many of them were isomers difficult to separate. Electrospray ionization techniques combined with multi-stage tandem spectrometry (MS^n) had the advantage of discriminating isobutylamides and 2-methylbutylamides[25]. Furthermore, isomeric alkamides could be distinguished by MS^n fragmentation patterns[28]. For isobutylamides the MS/MS spectra of deprotonated molecules (compounds **1**/**2**, **5**-**8**, **11**, **12**, and **13**/**14**) showed fragments corresponding to the loss of 56 u for the isobutyl group and 73 u for the isobutyl amine. Fragments corresponding to the loss of 70 u (for the 2-methylbutyl group) and 87 u (2-methylbutyl amine) could be observed for 2-methylbutylamides (compounds **3**/**4**, **9**/**10**, and **15**). In addition, diagnostic fragments corresponding to the alkyl chains due to the cleavage of the amide portions were detected (101 u for isobutylamides and 115 u for 2-methylbutylamides)[26,29].