SUPPLEMENTARY MATERIAL

Perspectives and challenges for direct analyses of proteins and secondary metabolites by mass spectrometry imaging (MSI) as pictured on sunflower trichomes

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1.1. UPLC-DAD-MS analyses of linear glandular trichomes

The LGT from central rib vein were manually collected, extracted with acetonitrile and diluted with water (9:1) for injection on UPLC-DAD-MS (the method is described in the manuscript- item 3.1). The chromatographic profile was illustrated in **Figure 1S** and the constituent data were summarized on **Table 1S**.

The metabolite identification was performed by injection of authentic standard (xanthomicrol) or from spectroscopic data (UV, MS and MS^2) data reported in the literature for *H. annuus* trichomes [14].

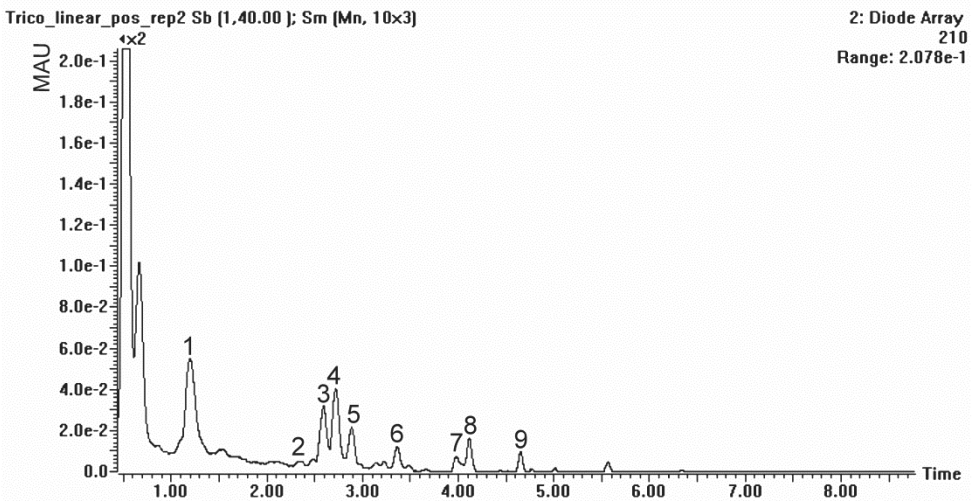

Figure S1. Chromatogram (at wavelength 210 nm) of an extract of sunflower linear glandular trichomes (LGT). For peak assignment see Table S1.

Table S1. Compound identification of chromatographic peaks (Figure S1) from the extract of sunflower linear trichomes and UV, MS and MS/MS data.

Peak	RT (min)	Compound	UV (nm)	Negative Mode (*m/z*)		Positive Mode (*m/z*)	
				MS $[M-H]^-$	MS/MS	MS $[M+H]^+$	MS/MS (eV)
1	1.30	Helibisabonol A	255, 280	267	-	269	-
2	2.49	Glandulone A	264	-	-	249	-
		Glandulone F		-	-	267	-
3	2.60	Demethoxysudachitin	269, 333	329	329 (20 eV)→314, 299, 240, 181, 143 329 (30 eV)→314, 299, 285, 279, 271, 268, 227, 211, 200, 179, 171, 145, 138, 117	331	331 (20 eV)→316, 301, 298, 273, 119 331 (30 eV)→316, 301, 285, 273, 241, 213, 181, 166, 155, 119
4	2.72	Acerosin	263, 334	359	359 (20 eV)→344, 329, 311, 298, 252, 213, 186, 119	361	361 (20 eV)→346, 331, 328 361 (30 eV)→346, 331, 328, 316, 301, 244, 227, 216, 193, 171, 151, 124
		Glandulone D	263	-	-	249	331 (20 eV)→316, 301, 271, 166, 109
5	2.88	Helibisabonol C/heliannuol A/ heliannuol D	290	-	-	251	251 (15 eV)→175, 163, 153, 127, 109, 71
6	3.35	Sideritiflavone	283	359	359 (20 eV)→344, 329, 311	361	361 (20 eV)→346, 331, 328, 313, 197, 135
7	3.97	Nevadensin	263, 336	343	343 (20 eV)→328, 313, 298	345	345 (20 eV)→330, 315, 297, 266, 227, 194 345 (30 eV)→315, 297, 284, 272, 227, 183, 155
8	4.12	Xanthomicrol	263, 333	343	343 (20 eV)→328, 313, 298	345	345 (20 eV)→330, 315, 297, 266, 227, 194 345 (30 eV)→315, 297, 284, 272, 227, 197, 179, 151, 119
		Methylsudachitin	281, 332	373	373 (20 eV)→358, 343, 328 343 (25 eV)→328, 313, 285, 241, 167, 152	375	375 (20 eV)→360, 345, 315 345 (20 eV)→330, 315, 284, 267, 213, 183, 135
9	4.65	Glandulone E	256	-	-	249	249 (15 eV)→231, 193, 163, 151, 109, 71

RT: retention time.

1.2. MALDI-MS analyses

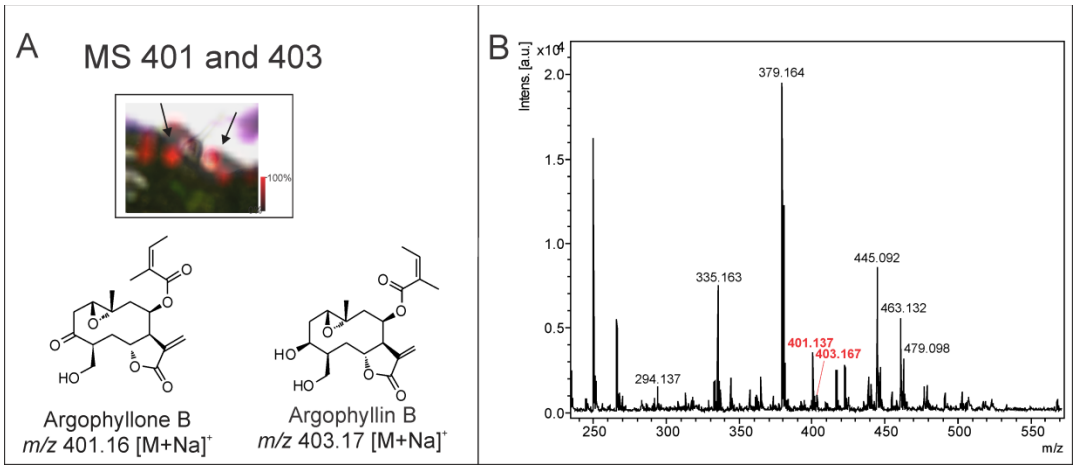

Figure S2. MALDI-MS image reconstructed from the ions *m/z* 403.17 and 401.16 $[M+Na]^+$ corresponding to argophyllin B and argophyllone B (**A**), respectively, and the mass spectrum from MSI highlighting these ions.

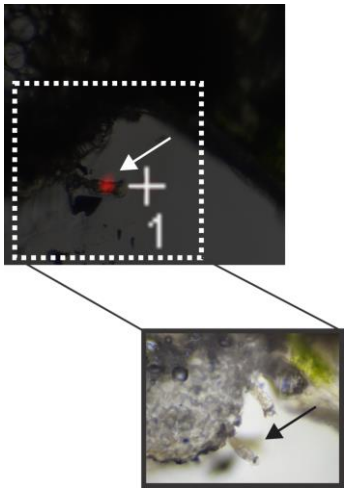

Figure S3. LDI-MS image reconstructed from ions *m/z* 329.06 (from demethoxysudachitin), 343.08 (nevadensin/xanthomicrol), 359.08 (sideritiflavone) and 373.09 $[M-H]^-$(methylsudachitin), highlighting the linear glandular trichome (LGT). The arrow indicates the LGT analyzed.