Development of "Laser Ablation Direct Analysis in Real Time Imaging" Mass Spectrometry (LADI-MS): Application to Spatial Distribution Mapping of Metabolites Along the Biosynthetic Cascade Leading to Synthesis of Atropine and Scopolamine in Plant Tissue

SUPPORTING INFORMATION

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This document contains Table S1 which lists mass measurement data for a typical DART-HRMS analysis of a *Datura leichhardtii* seed acquired in positive ion mode. The mass spectrum to which it corresponds is shown in Figure 4. Also within this document are the MALDI-MS/MS SpiralTOF mass spectra for confirmation of the presence of the ions depicted in Figure 4 (Figures S1-S6).

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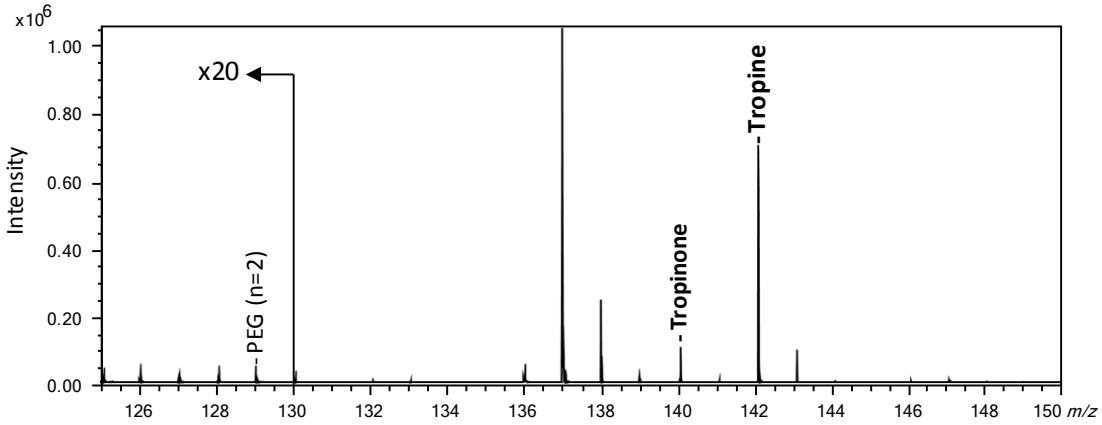
Supporting Information Table S1. DART-MS mass measurement data for the ions featured in this work.

Compound*	Composition	Observed Mass	Calculated Mass	Difference (mmu)
Unknown identity peak	-	124.1124	-	-
Unknown identity peak	-	131.0465	-	-
Tropinone	$C_8H_{13}NO + H^+$	140.1079	140.1075	0.4
Tropine	$C_8H_{15}NO + H^+$	142.1197	142.1232	3.5
Unknown identity peak	-	163.0742	-	-
Unknown identity peak	-	174.1124	-	
Arginine	$C_6H_{14}N_4O_2 + H^+$	175.1217	175.1195	2.2
Unknown identity peak	-	179.0695	-	-
Unknown identity peak	-	197.0820	-	-
Atropine	$C_{17}H_{23}NO_3 + H^+$	290.1744	290.1756	1.2
Littorine[§]	$C_{17}H_{23}NO_3 + H^+$	290.1744	290.1756	1.2
Scopolamine	$C_{17}H_{21}NO_4 + H^+$	304.1552	304.1549	0.3
Unknown identity peak[‡]	-	381.3340	-	-

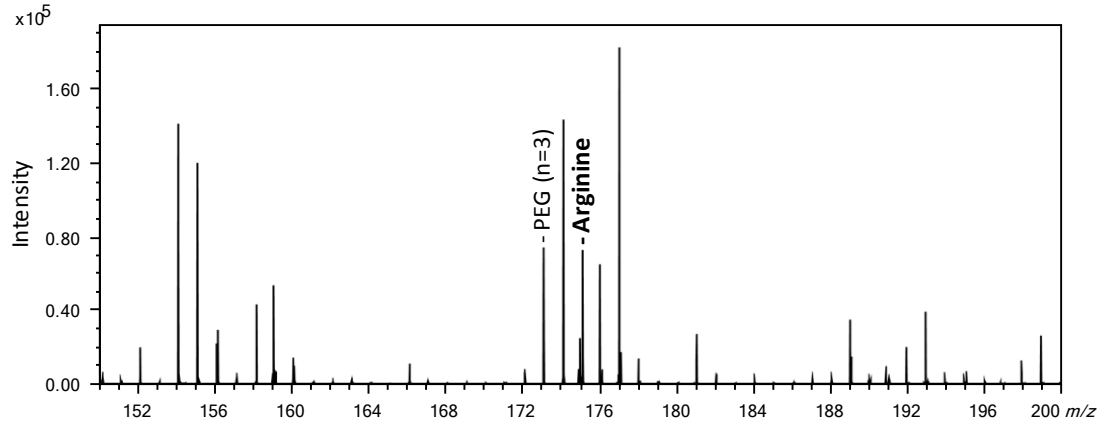
*Unless otherwise stated, peaks of unknown identity that are listed are those of abundance ≥ 9.2% relative to the base peak. [§]Assignment is tentative. [‡]Spatial distribution of this mass was confined to the embryo and half of the seed coat.

Supporting Information Figure S1. MALDI mass spectra of an aqueous extract of the seed with PEG 200 as a calibrant. Peaks corresponding to tropinone, tropine, arginine, scopolamine and atropine are shown. Panels A, B, and C show the indicated mass ranges.

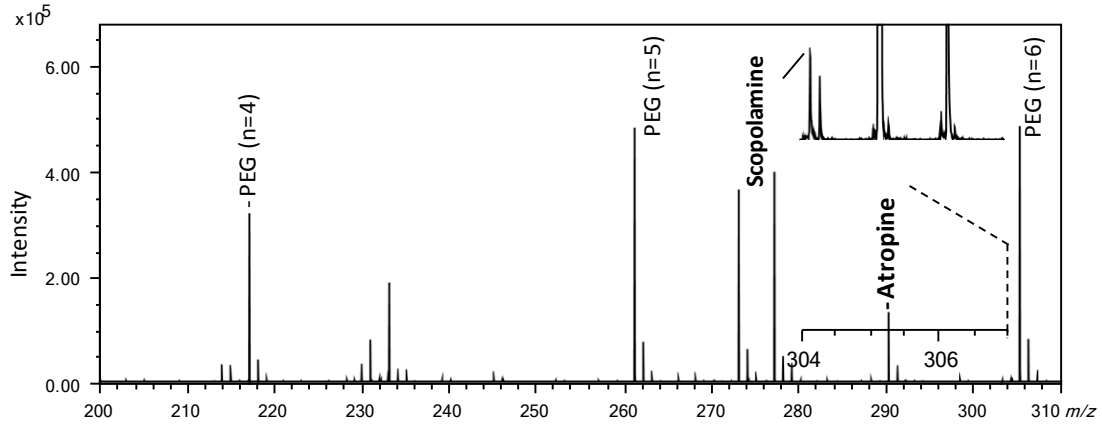
Panel A



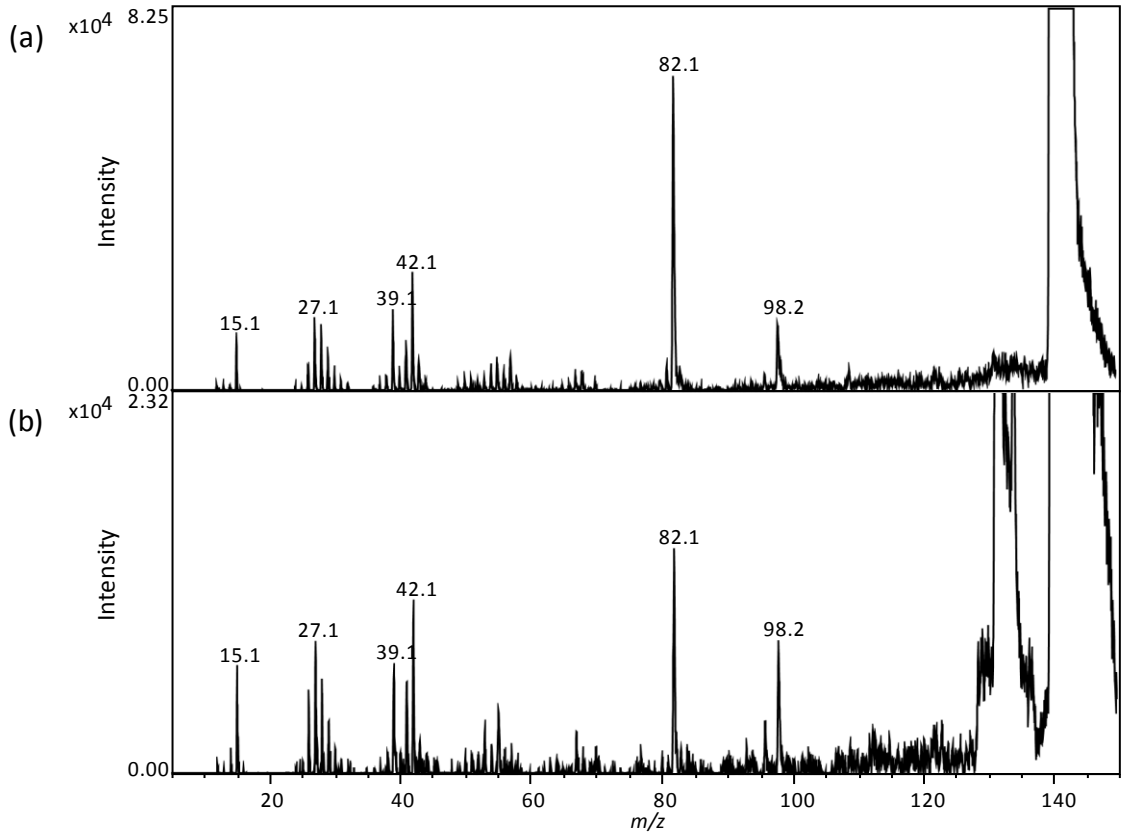
Panel B



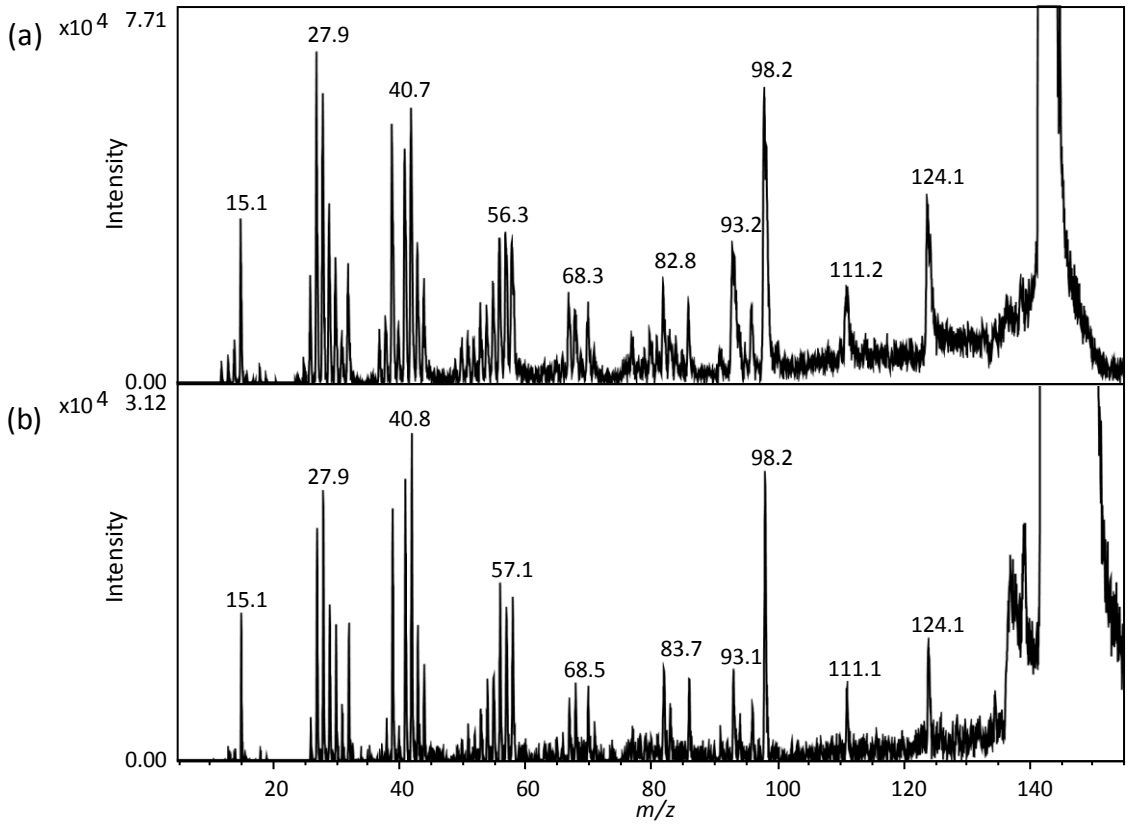
Panel C



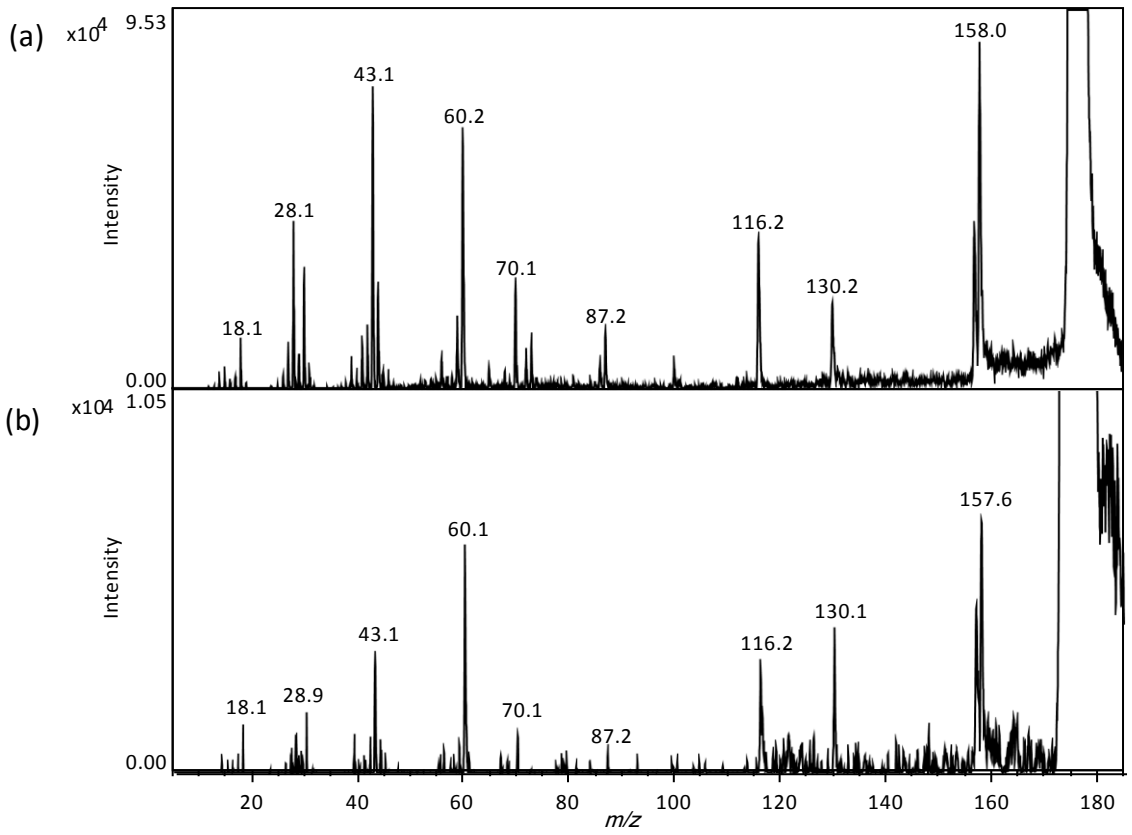
Supporting Information Figure S2. Product-ion spectra for tropinone (*m/*z 140.1) authentic standard solution (a) and aqueous seed extract (b).



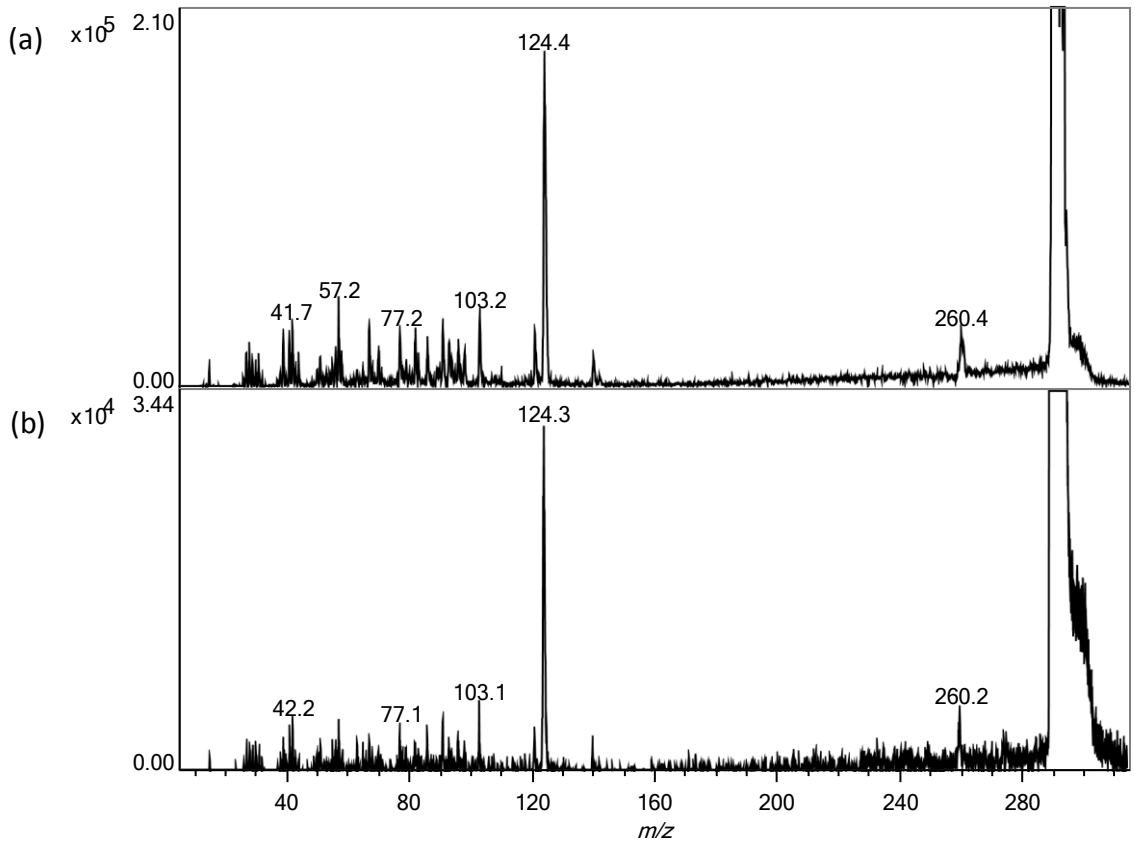
Supporting Information Figure S3. Product-ion spectra for tropine (*m/z* 142.1) authentic standard solution (a) and aqueous seed extract (b).



Supporting Information Figure S4. Product-ion spectra for arginine (*m/z* 175.1) authentic standard solution (a) and aqueous seed extract (b).



Supporting Information Figure S5. Product-ion spectra for atropine (*m/z* 290.2) authentic standard solution (a) and aqueous seed extract (b).



Supporting Information Figure S6. Product-ion spectra for scopolamine (*m/z* 304.2) authentic standard solution (a) and aqueous seed extract (b).