Plant Seed Species Identification from Chemical Fingerprints—A High-Throughput Application of Direct Analysis in Real Time Mass Spectrometry

SUPPLEMENTARY INFORMATION

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This document contains twelve additional figures and fourteen tables of supporting information associated with the entitled article. The figures show the vacuum tweezer apparatus, the DART-MS in-source CID spectra used for confirmation of the presence of alkaloids, and DART-MS spectra of *Datura* spp. seed extracts prepared using 6 different solvents. The tables contain information on the seed spectra including accurate masses and relative abundances of various peaks, the feature masses used for LDA classification, and calculated RSD values for eight diagnostic alkaloids.

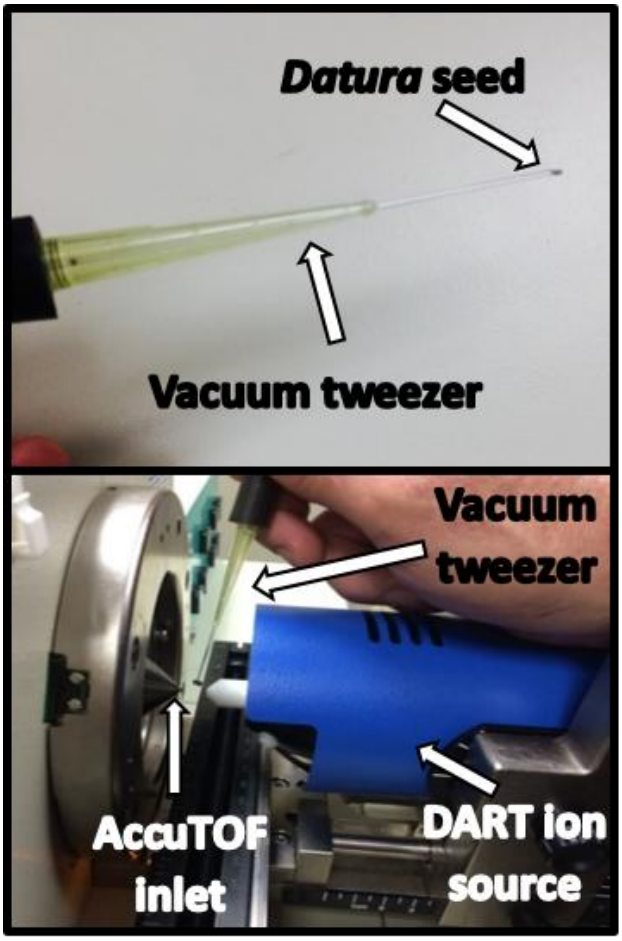

Figure S-1. Analysis of a *Datura* seed by DART-HR-TOF-MS using the vacuum tweezer apparatus. The top panel shows the tweezer apparatus. The bottom panel shows the placement of the apparatus between the DART ion source and the mass spectrometer inlet. A seed was sliced in half and held between the DART ion source and the AccuTOF-MS inlet using the tweezer.

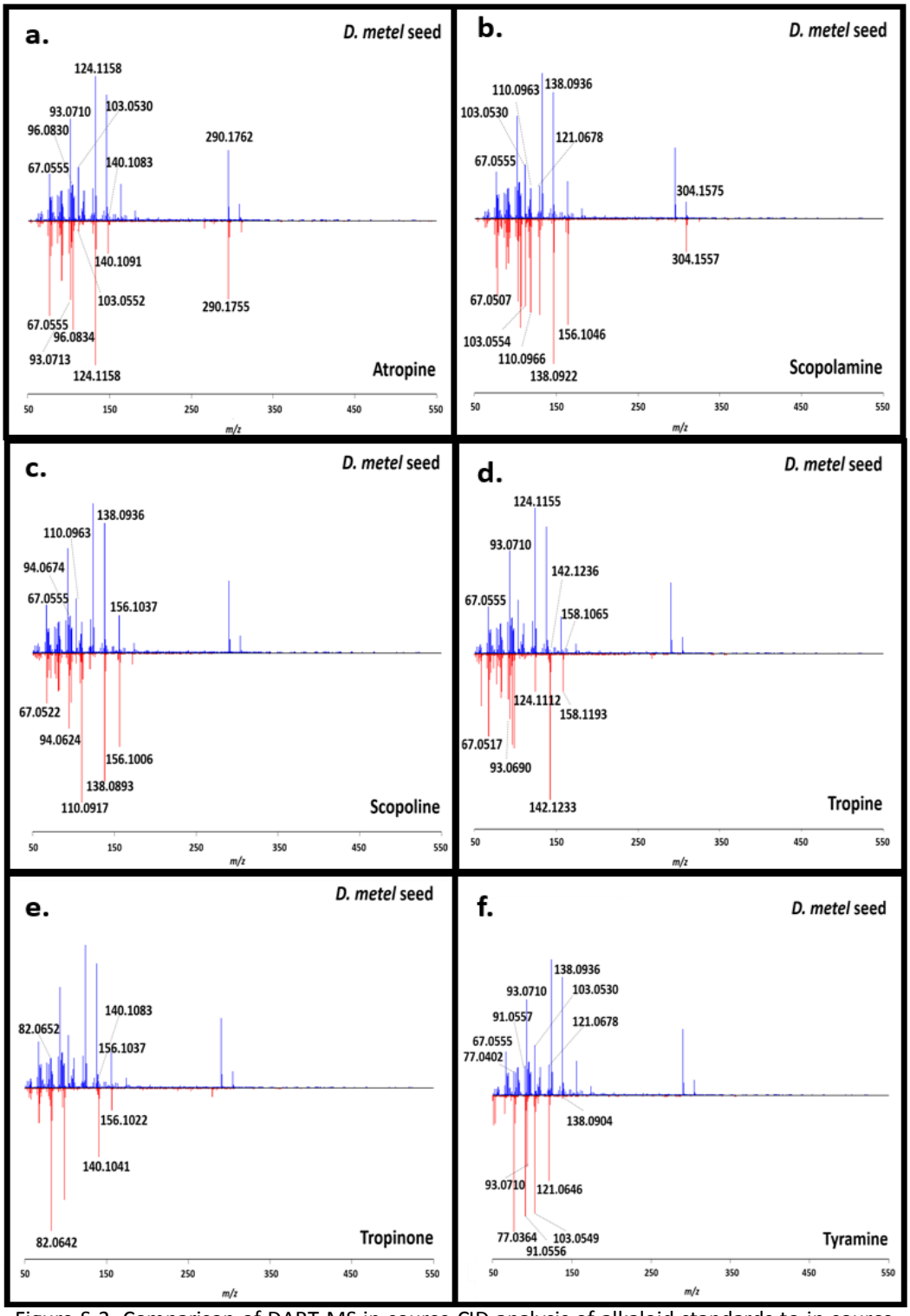

Figure S-2. Comparison of DART-MS in-source CID analysis of alkaloid standards to in-source CID analysis of a *D. metel* seed, rendered as heat-to-tail plots. In-source CID spectra were collected at a 90 V cone voltage. In each panel, the top spectrum represents in-source CID of the seed, and the bottom one shows in-source CID of the indicated alkaloid standard. The head-to-tail plots show that the fragments observed in the standard are present in the in-source CID spectrum of the seed. Panel a: atropine standard; Panel b: scopolamine standard; Panel c: scopoline standard; Panel d: tropine standard; Panel e: tropinone standard; Panel f: tyramine standard.

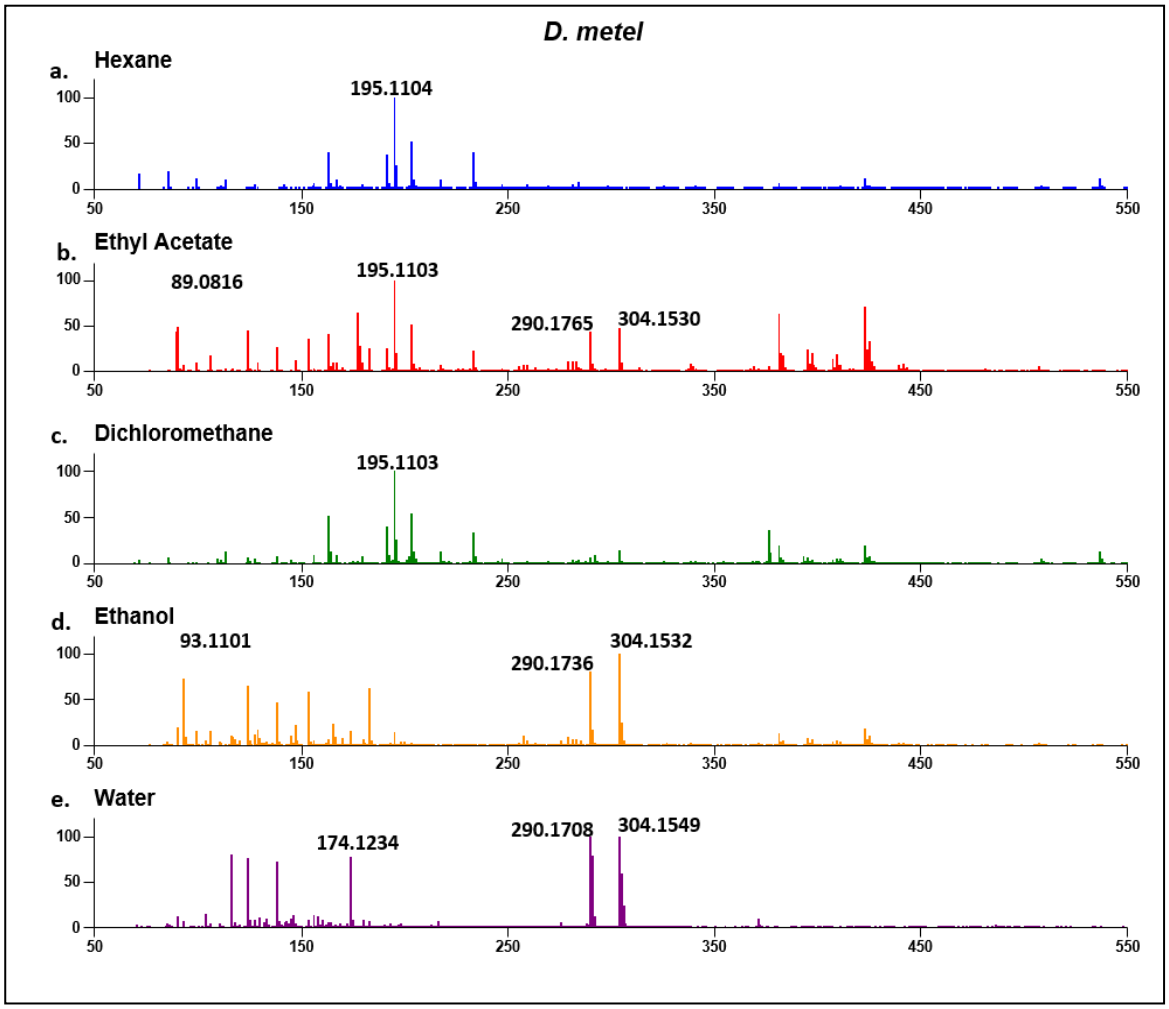

Figure S-3. DART-HR-TOF-MS spectra of the indicated extracts of *D. metel* seeds. Solvents of increasing dielectric constant were used to determine the optimal solvent extraction system for detection of the diagnostic alkaloids. Panel a: hexane extract; Panel b: ethyl acetate extract; Panel c: dichloromethane extract. Panel d: ethanol extract; Panel e: water extract. Mass measurement data associated with each spectrum are listed in Supplementary Information Table S-3.

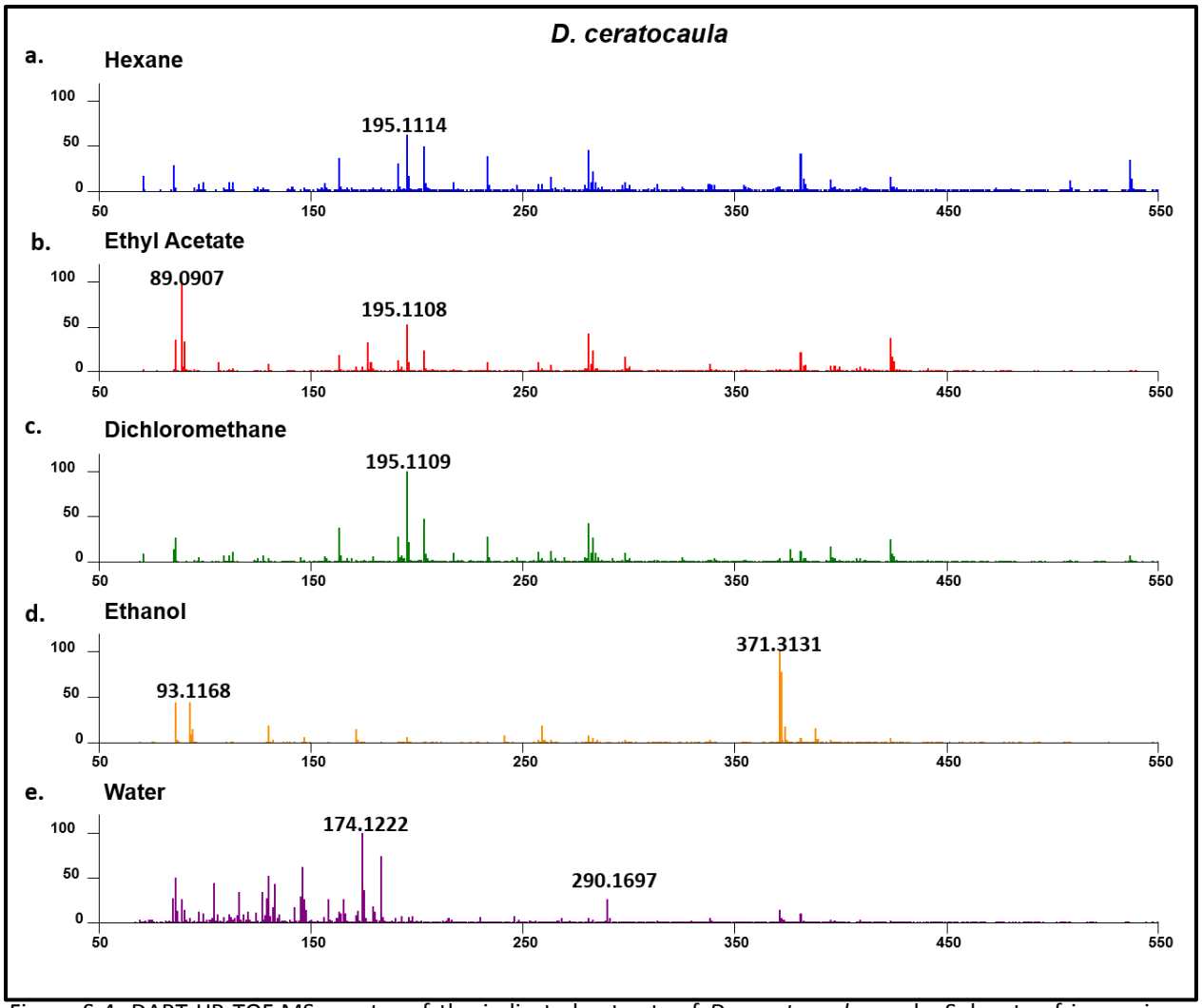

Figure S-4. DART-HR-TOF-MS spectra of the indicated extracts of *D. ceratocaula* seeds. Solvents of increasing dielectric constant were used to determine the optimal solvent extraction system for detection of the diagnostic alkaloids. Panel a: hexane; Panel b: ethyl acetate; Panel c: dichloromethane; Panel d: ethanol; Panel e: water. Mass measurement data associated with each spectrum are listed in Supplementary Information Table S-4.

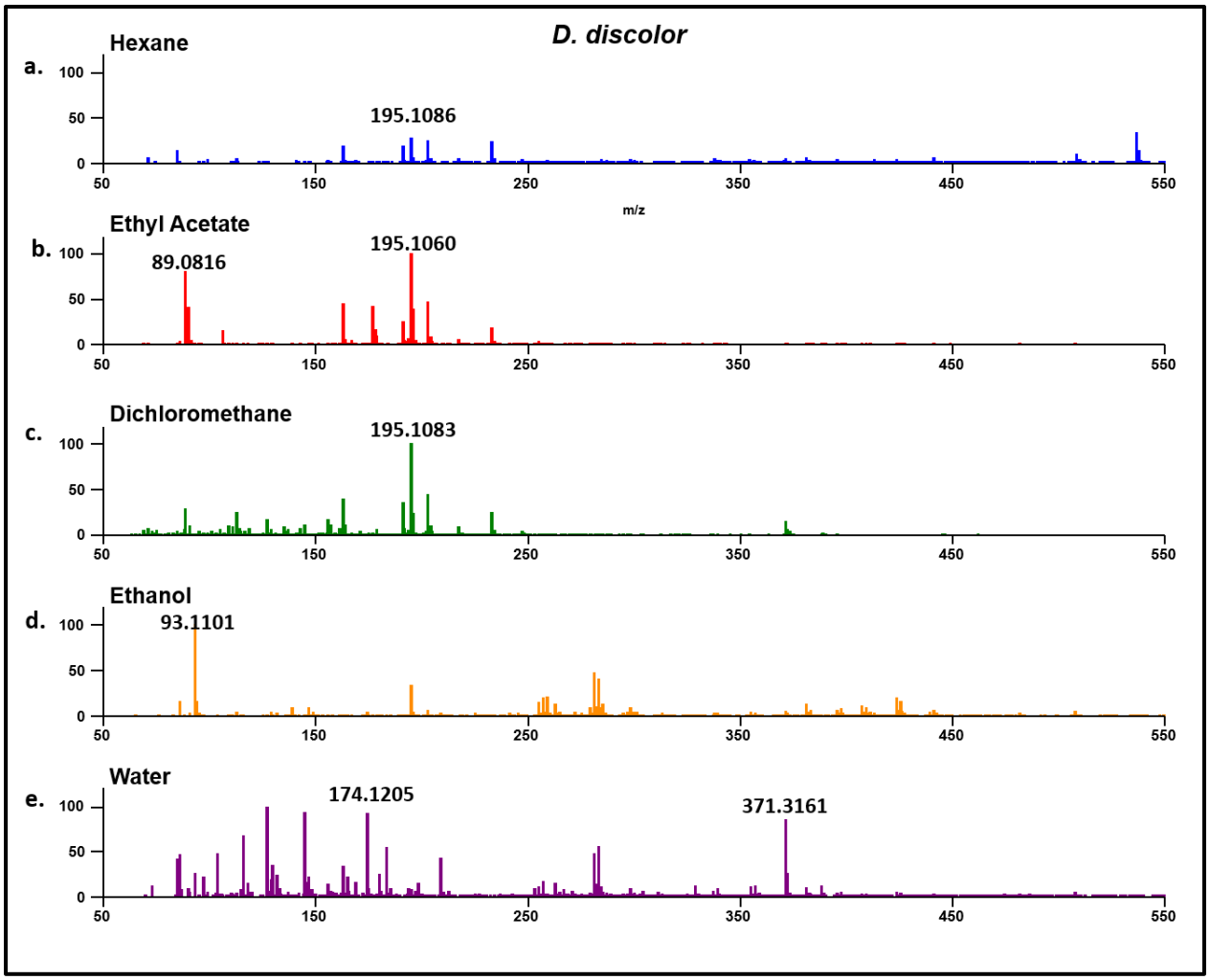

Figure S-5. DART-HR-TOF-MS spectra of the indicated extracts of *D. discolor* seeds. Solvents of increasing dielectric constant were used to determine the optimal solvent extraction system for detection of the diagnostic alkaloids. Panel a: hexane; Panel b: ethyl acetate; Panel c: dichloromethane; Panel d: ethanol; Panel e: water. Mass measurement data associated with each spectrum are listed in Supplementary Information Table S-5.

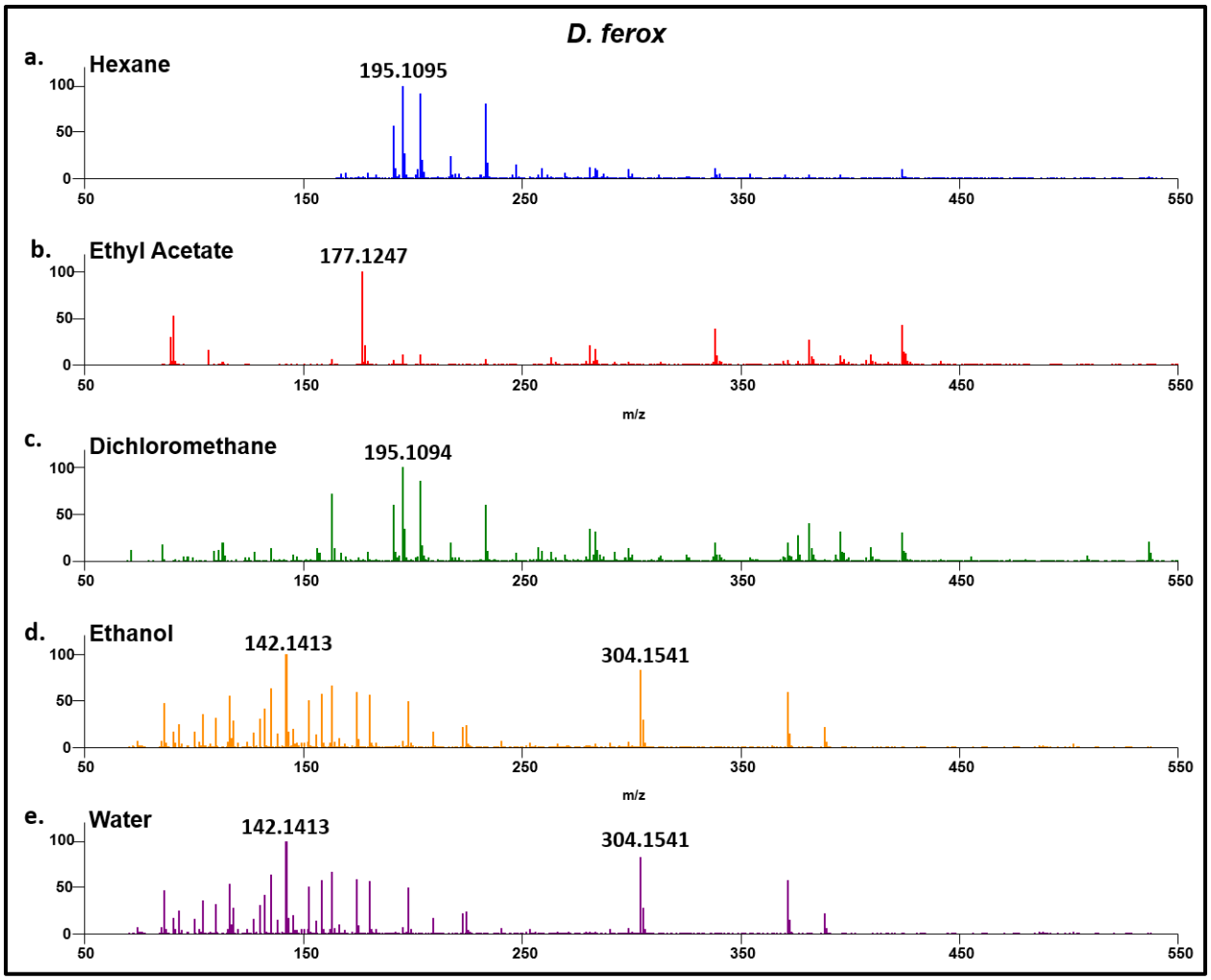

Figure S-6. DART-HR-TOF-MS spectra of the indicated extracts of *D. ferox* seeds. Solvents of increasing dielectric constant were used to determine the optimal solvent extraction system for detection of the diagnostic alkaloids. Panel a: hexane; Panel b: ethyl acetate; Panel c: dichloromethane; Panel d: ethanol; Panel e: water. Mass measurement data associated with each spectrum are listed in Supplementary Information Table S-6.

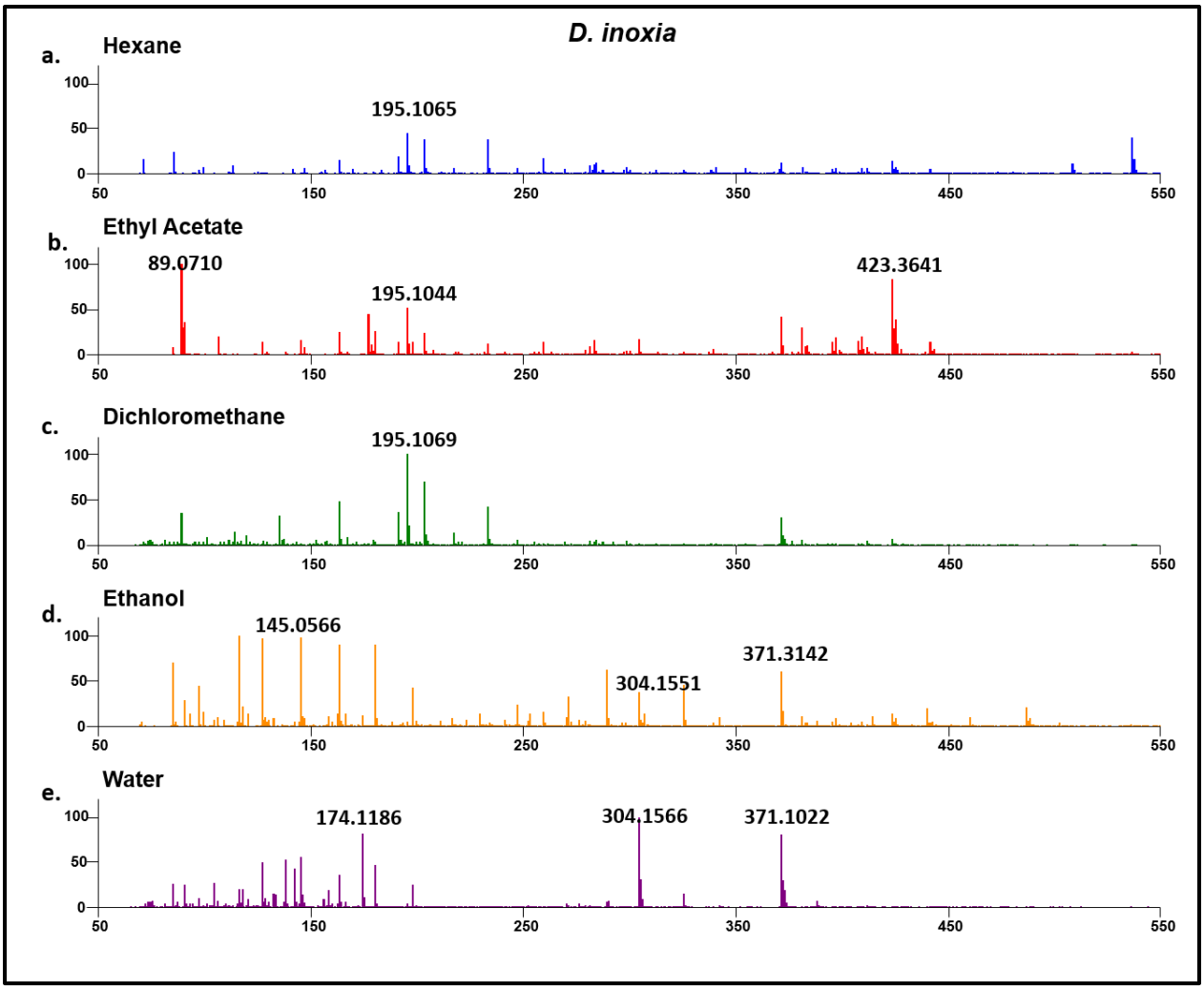

Figure S-7. DART-HR-TOF-MS spectra of the indicated extracts of *D. inoxia* seeds. Solvents of increasing dielectric constant were used to determine the optimal solvent extraction system for detection of the diagnostic alkaloids. Panel a: hexane; Panel b: ethyl acetate; Panel c: dichloromethane; Panel d: ethanol; Panel e: water. Mass measurement data associated with each spectrum are listed in Supplementary Information Table S-7.

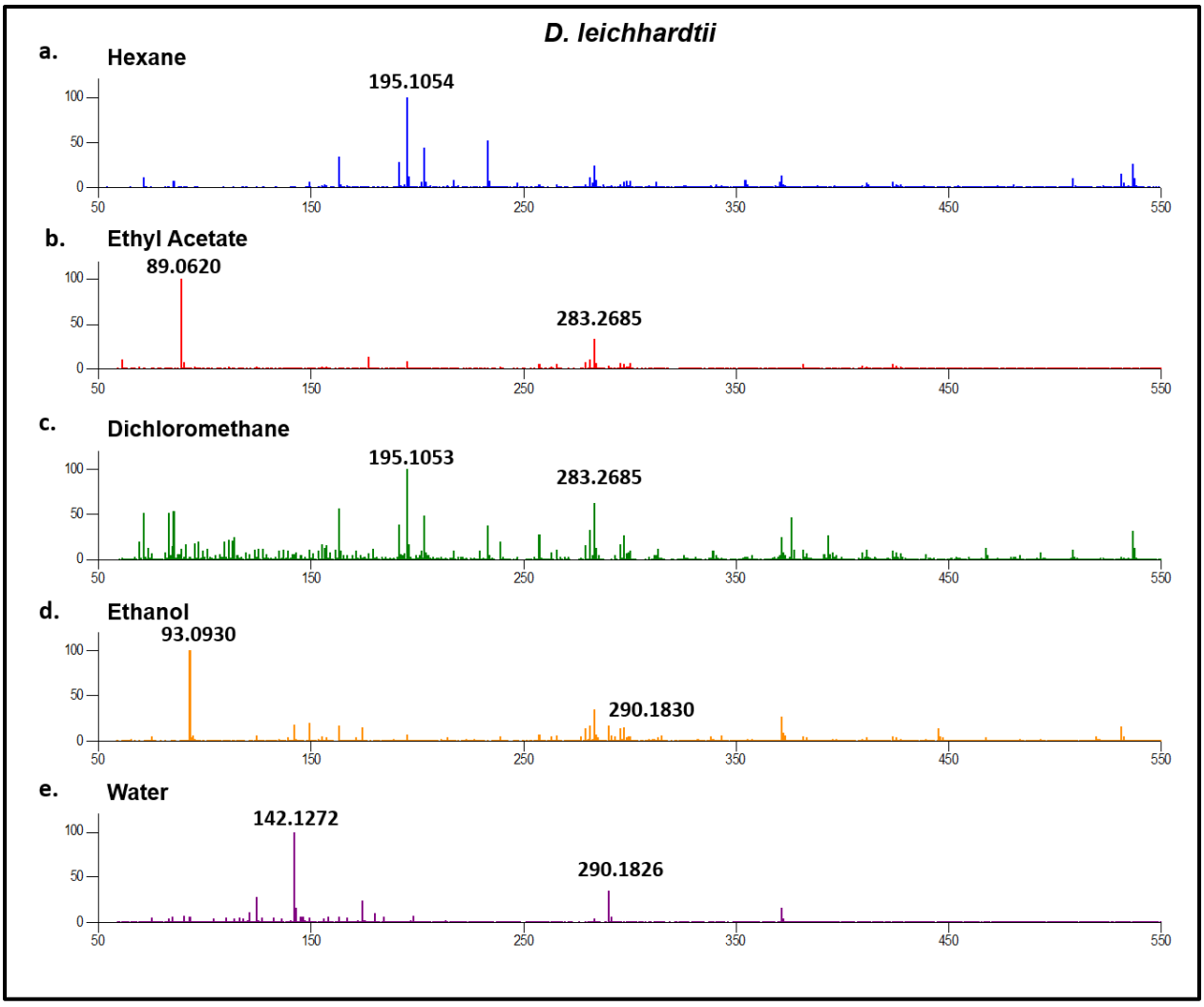

Figure S-8. DART-HR-TOF-MS spectra of the indicated extracts of *D. leichhardtii* seeds. Solvents of increasing dielectric constant were used to determine the optimal solvent extraction system for detection of the diagnostic alkaloids. Panel a: hexane; Panel b: ethyl acetate; Panel c: dichloromethane; Panel d: ethanol; Panel e: water. Mass measurement data associated with each spectrum are listed in Supplementary Information Table S-8.

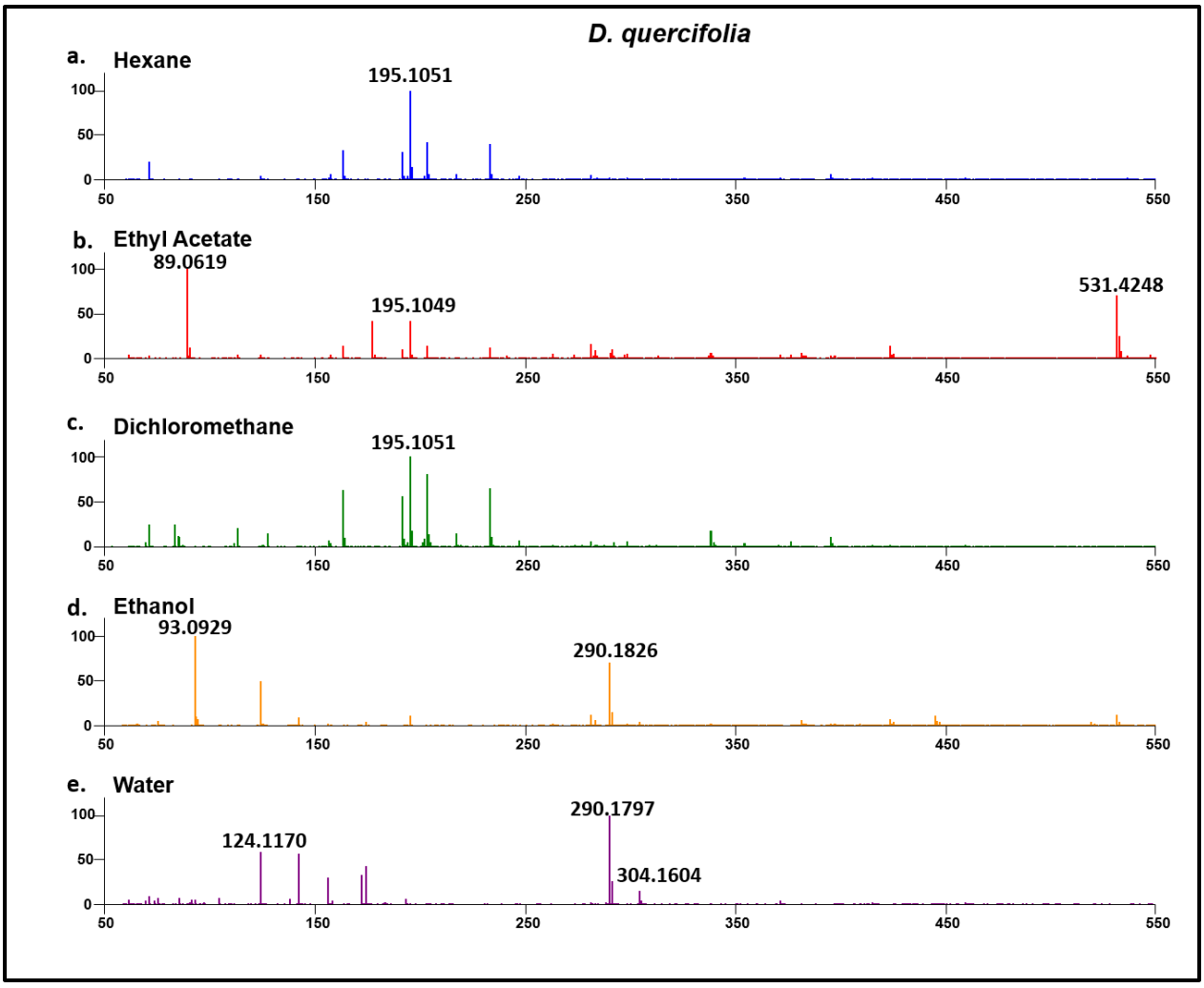

Figure S-9. DART-HR-TOF-MS spectra of the indicated extracts of *D. quercifolia* seeds. Solvents of increasing dielectric constant were used to determine the optimal solvent extraction system for detection of the diagnostic alkaloids. Panel a: hexane; Panel b: ethyl acetate; Panel c: dichloromethane; Panel d: ethanol; Panel e: water. Mass measurement data associated with each spectrum are listed in Supplementary Information Table S-9.

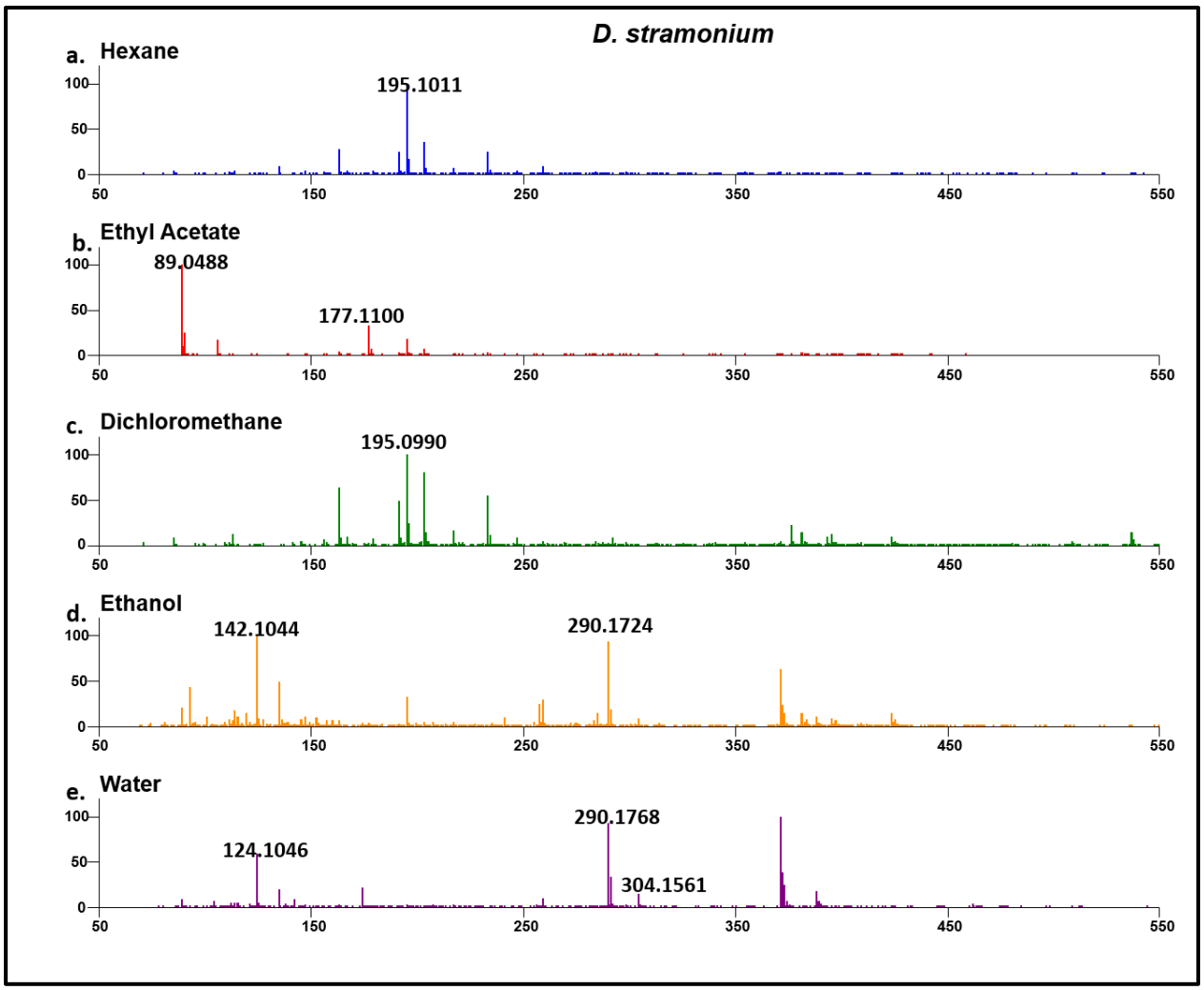

Figure S-10. DART-HR-TOF-MS spectra of the indicated extracts of *D. stramonium* seeds. Solvents of increasing dielectric constant were used to determine the optimal solvent extraction system for detection of the diagnostic alkaloids. Panel a: hexane; Panel b: ethyl acetate; Panel c: dichloromethane; Panel d: ethanol; Panel e: water. Mass measurement data associated with each spectrum are listed in Supplementary Information Table S-10.

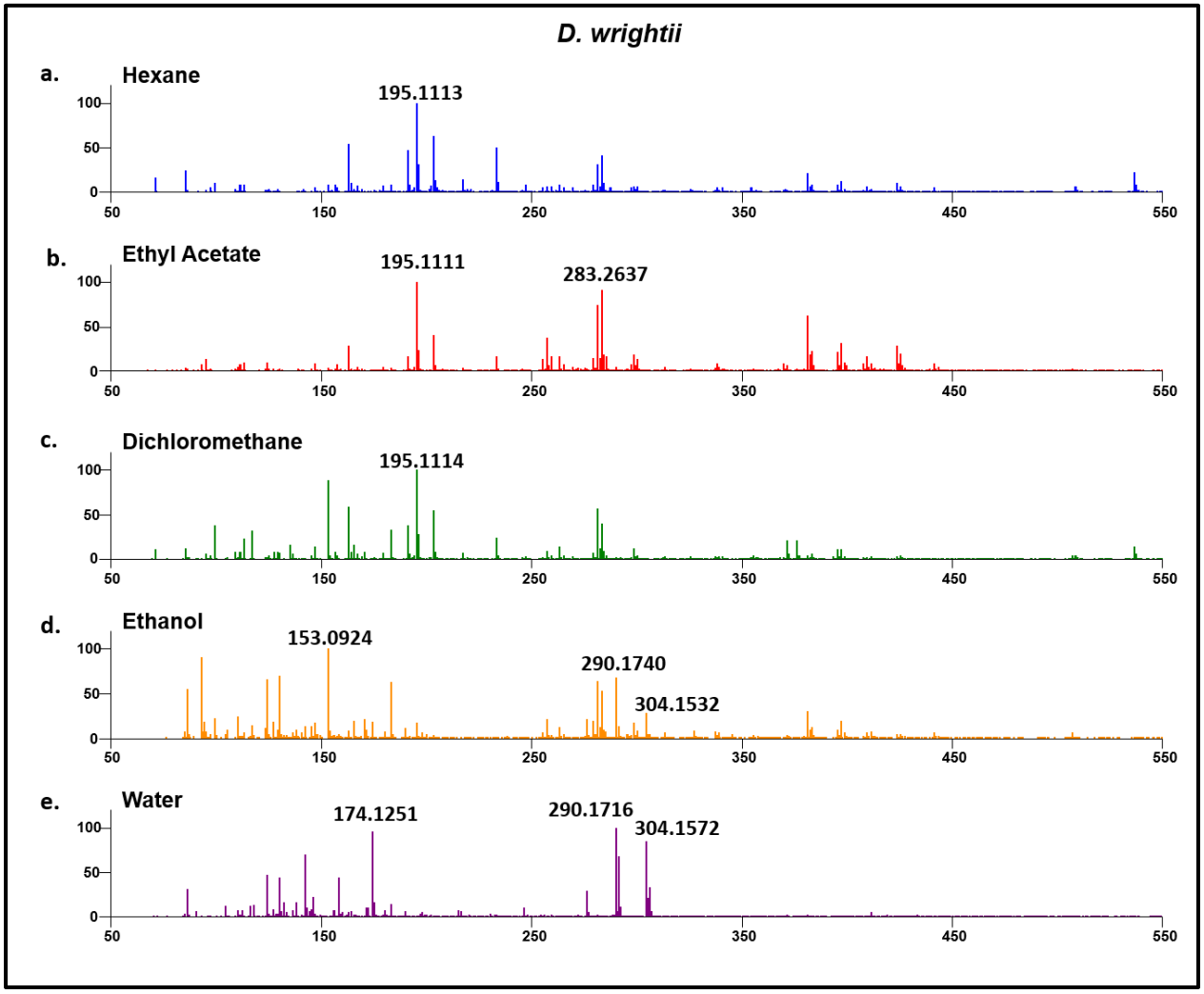

Figure S-11. DART-HR-TOF-MS spectra of the indicated extracts of *D. wrightii* seeds. Solvents of increasing dielectric constant were used to determine the optimal solvent extraction system for detection of the diagnostic alkaloids. Panel a: hexane; Panel b: ethyl acetate; Panel c: dichloromethane; Panel d: ethanol; Panel e: water. Mass measurement data associated with each spectrum are listed in Supplementary Information Table S-11.

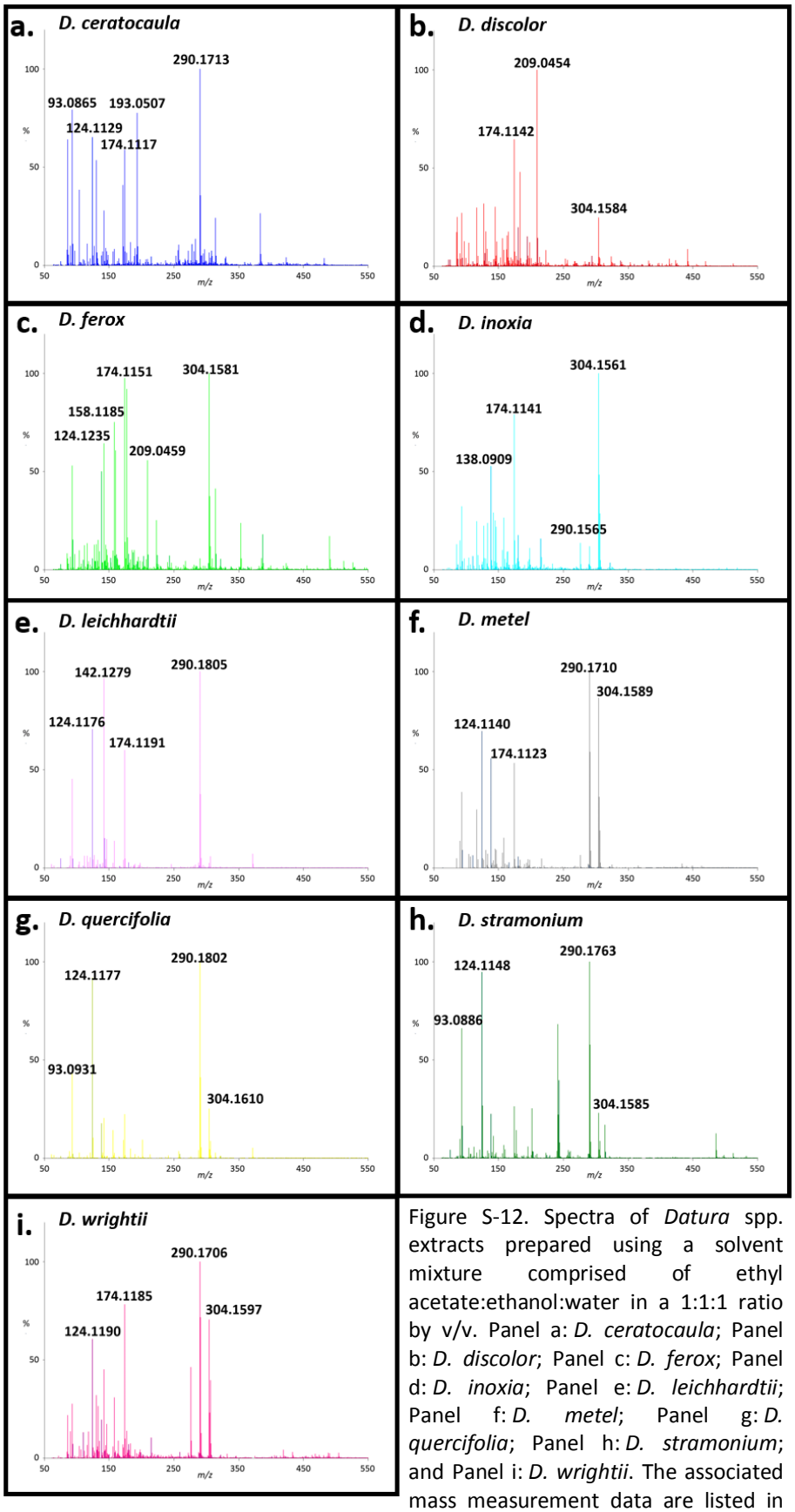

Figure S-12. Spectra of *Datura* spp. extracts prepared using a solvent mixture comprised of ethyl acetate:ethanol:water in a 1:1:1 ratio by v/v. Panel a: *D. ceratocaula*; Panel b: *D. discolor*; Panel c: *D. ferox*; Panel d: *D. inoxia*; Panel e: *D. leichhardtii*; Panel f: *D. metel*; Panel g: *D. quercifolia*; Panel h: *D. stramonium*; and Panel i: *D. wrightii*. The associated mass measurement data are listed in Supplementary Information Table S-12.

Table S-1: Relative abundances for peaks at the indicated nominal *m/z* values that were detected at ≥ 10% abundance unless otherwise indicated.[a,b] The corresponding spectra appear in Figure 2.

m/z	*D. ceratocaula*	*D. discolor*	*D. ferox*	*D. inoxia*	*D. leichhardtii*	*D. metel*	*D. quercifolia*	*D. stramonium*	*D. wrightii*
72				11.4					21.9
74		23.2		19.1	10.1		11.4	10.0	32.5
86	57.6	44.6	10.2						100.0
90									12.0
96				22.5					
104	42.8	21.4	11.0				15.2		12.1
110	14.4	10.9							22.2
114							14.6		
116	15.3	17.8							
122	66.1								
124	13.1				17.5	47.5	30.6	68.6	
125									12.5
127		10.4		26.8		10.8			
130	13.5	16.9		11.5					23.3
135	11.0	10.3					17.7		
138				31.9		47.9		11.4	
140	6.1			2.5		2.1	3.9		
142	64.7	4.7	100.0	20.9	58.8	4.8	79.7	24.9	36.2
143			15.2				12.6		
144				15.2					
145		10.9		25.4		11.6			
153	10.8					27.9	17.4		15.0
156	6.5	3.3	3.8	15.9	2.3	7.7	20.4	2.8	5.4
158	38.6	14.0	60.0	36.2	10.3	9.3	12.7	12.1	14.4
163	17.8	14.8		13.1	21.7	14.9			
171									27.5
174	100.0	100.0	79.6	81.2	96.5	38.6	85.9	45.0	44.3
175	24.4	13.0	12.1	11.5	13.1				
179	15.0	16.0			11.7	10.8			
180		11.0		19.1		10.3			
183	19.3					18.6	17.0		
190	10.2								
192	18.8								
193	96.1								
194	10.8								
209	20.6	11.0	18.3						
224			12.3						
241								18.2	
257	11.3				55.9				
263	12.5								
272		11.3				11.5	18.4	12.2	
274					23.0				
279	10.3				12.3				
281	39.2		10.2		12.3		10.7		
283	33.2		10.6		33.6				
290	54.3			12.4	100.0	100.0	100.0	100.0	67.1
291	11.6				28.4	51.7	43.7	33.4	19.8
295	10.5				11.9				
297	20.4				10.1				
298	47.5		25.5		14.8		24.9		15.5
299	12.9								
300	23.7		12.7		22.7				10.1
304	4.0		22.3	100.0		86.0	19.1	19.2	38.6
305				30.8		32.9			

306				19.2		12.4			
314	24.4								
338							13.3		12.6
381	12.6								
383	10.1								
395	13.3								
397	11.9								
413		29.0							
415	14.6								
423	37.0	15.0	11.3				15.2		
424	12.7								
425	10.8								
429	13.8								
441		54.0							10.6
445	12.4								
448		11.2							
469		17.3							
476		23.0							10.2

[a]Peaks at nominal *m/z* values of 138, 140, 142, 156, 158, 174, 290, and 304 represent tyramine, tropinone, tropine, scopoline, dihydroxytropane, trihydroxytropane, atropine/hyoscyamine, and scopolamine/hyoscine respectively, as determined through comparison of the in-source CID data of authentic standards with the in-source CID seed spectra recorded under identical conditions.

[b]Peaks at nominal *m/z* 138, 140, 142, 156, 158, 174, 290, and 304 represent diagnostic alkaloids that were observed above a 2% threshold.

Table S-2. Accurate *m/z* values from positive-ion mode DART-HR-TOF-MS spectral data of *Datura* seeds from Figure 2, highlighting the alkaloids whose presence was confirmed.

Species Name	Compound[a]	Composition	Adduct	Measured Mass	Calculated Mass	Difference (mmu)[b]	Abund.
D. ceratocaula	Tropine	$C_8H_{15}NO$	$+H^+$	142.1190	142.1232	4.2	68.5
	Dihydroxytropane	$C_8H_{15}NO_2$	$+H^+$	158.1161	158.1181	2.0	65.6
	Trihydroxytropane	$C_8H_{15}NO_3$	$+H^+$	174.1086	174.1130	4.4	100.0
	Scopoletine	$C_{10}H_8O_4$	$+H^+$	193.0475	193.0501	2.6	81.0
	Atropine	$C_{17}H_{23}NO_3$	$+H^+$	290.1720	290.1756	3.6	14.4
D. discolor	Dihydroxytropane	$C_8H_{15}NO_2$	$+H^+$	158.1148	158.1181	3.3	18.0
	Trihydroxytropane	$C_8H_{15}NO_3$	$+H^+$	174.1102	174.1130	2.8	100.0
	Scopolamine	$C_{17}H_{21}NO_4$	$+H^+$	304.1534	304.1549	1.5	2.8
D. ferox	Tyramine	$C_8H_{11}NO$	$+H^+$	138.0888	138.0919	3.1	3.9
	Tropine	$C_8H_{15}NO$	$+H^+$	142.1211	142.1232	2.1	100.0
	Scopoline	$C_8H_{13}NO$	$+H^+$	156.0989	156.1025	3.6	4.1
	Dihydroxytropane	$C_8H_{15}NO_2$	$+H^+$	158.1155	158.1181	2.6	69.0
	Trihydroxytropane	$C_8H_{15}NO_3$	$+H^+$	174.1110	174.1130	2.0	74.1
	Scopolamine	$C_{17}H_{21}NO_4$	$+H^+$	304.1506	304.1549	4.3	52.7
D. inoxia	Tyramine	$C_8H_{11}NO$	$+H^+$	138.0883	138.0919	3.6	13.2
	Tropinone	$C_8H_{13}NO$	$+H^+$	140.1057	140.1075	1.8	28.2
	Scopoline	$C_8H_{13}NO$	$+H^+$	156.1000	156.1025	2.5	31.8
	Trihydroxytropane	$C_8H_{15}NO_3$	$+H^+$	174.1099	174.1130	3.1	100.0
	Atropine	$C_{17}H_{23}NO_3$	$+H^+$	290.1712	290.1756	4.4	61.9
	Scopolamine	$C_{17}H_{21}NO_4$	$+H^+$	304.1523	304.1549	2.6	70.0
D. leichhardtii	Tropine	$C_8H_{13}NO$	$+H^+$	142.1199	142.1232	3.3	58.9
	Vanillin	$C_8H_8O_3$	$+H^+$	153.0575	153.0552	2.3	2.0
	Scopoline	$C_8H_{13}NO$	$+H^+$	156.0984	156.1025	4.0	2.3
	Dihydroxytropane	$C_8H_{15}NO_2$	$+H^+$	158.1150	158.1181	3.1	10.3
	Trihydroxytropane	$C_8H_{15}NO_3$	$+H^+$	174.1120	174.1130	1.0	96.5
	Atropine	$C_{17}H_{23}NO_3$	$+H^+$	290.1751	290.1756	0.5	100.0
D. metel	Tyramine	$C_8H_{11}NO$	$+H^+$	138.0919	138.0919	0.0	19.9
	Scopoline	$C_8H_{13}NO$	$+H^+$	156.1008	156.1025	1.7	6.7
	Dihydroxytropane	$C_8H_{15}NO_2$	$+H^+$	158.1138	158.1181	4.3	8.9
	Trihydroxytropane	$C_8H_{15}NO_3$	$+H^+$	174.1129	174.1130	0.1	30.5
	Atropine	$C_{17}H_{23}NO_3$	$+H^+$	290.1759	290.1756	0.3	100.0
	Scopolamine	$C_{17}H_{21}NO_4$	$+H^+$	304.1548	304.1549	0.1	97.0
D. quercifolia	Tyramine	$C_8H_{11}NO$	$+H^+$	138.0883	138.0919	3.6	5.0
	Tropine	$C_8H_{15}NO$	$+H^+$	142.1219	142.1232	1.3	79.7
	Scopoline	$C_8H_{13}NO$	$+H^+$	156.1015	156.1025	1.0	20.4
	Dihydroxytropane	$C_8H_{15}NO_2$	$+H^+$	158.1142	158.1181	3.9	12.7
	Trihydroxytropane	$C_8H_{15}NO_3$	$+H^+$	174.1126	174.1130	0.4	85.9
	Atropine	$C_{17}H_{23}NO_3$	$+H^+$	290.1756	290.1756	0.2	100.0
	Scopolamine	$C_{17}H_{21}NO_4$	$+H^+$	304.1571	304.1749	2.2	19.1

D. stramonium	Tyramine	$C_8H_{11}NO$	$+H^+$	138.0906	138.0919	1.3	17.4
	Tropine	$C_8H_{13}NO$	$+H^+$	142.1195	142.1232	3.7	28.2
	Dihydroxytropane	$C_8H_{15}NO_2$	$+H^+$	158.1138	158.1181	4.3	14.5
	Trihydroxytropane	$C_8H_{15}NO_3$	$+H^+$	174.1103	174.1130	2.7	53.2
	Atropine	$C_{17}H_{23}NO_3$	$+H^+$	290.1720	290.1756	3.6	100.0
	Scopolamine	$C_{17}H_{21}NO_4$	$+H^+$	304.1540	304.1549	0.9	29.6
D. wrightii	Tropine	$C_8H_{13}NO$	$+H^+$	142.1188	142.1232	4.4	29.6
	Dihydroxytropane	$C_8H_{15}NO_2$	$+H^+$	158.1135	158.1181	4.6	12.9
	Trihydroxytropane	$C_8H_{15}NO_3$	$+H^+$	174.1103	174.1130	2.7	45.1
	Atropine	$C_{17}H_{23}NO_3$	$+H^+$	290.1722	290.1756	3.4	90.2
	Scopolamine	$C_{17}H_{21}NO_4$	$+H^+$	304.1527	304.1549	2.2	100.0

[a]Compound identities were confirmed through comparison of the peaks observed in in-source CID analysis of authentic standards to those detected in in-source CID analysis of the seeds under identical conditions. [b]Measured masses fell within 5 mmu of the calculated masses.

Table S-3: Positive-ion mode DART-MS measurements for nominal masses with relative abundances above a 10% threshold for *D. metel* extracts prepared using the indicated solvents. The corresponding spectra appear in Supplementary Information Figure S-3.

Hexane		**Ethyl acetate**		**Dichloromethane**		**Ethanol**		**Water**	
m/z	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**
71	16.3	89	43.4	113	11.7	90	19.3	90	12.0
85	18.3	90	48.1	163	51.4	93	72.4	104	14.7
99	11.1	106	17.4	164	11.6	99	15.5	116	79.8
163	40.9	124	44.4	191	39.0	106	14.1	124	75.9
191	36.8	138	26.7	195	100.0	124	64.7	130	11.8
195	100.0	147	11.2	196	24.9	127	10.7	138	71.4
196	25.8	153	35.4	203	53.1	129	17.4	146	13.8
203	52.2	163	40.7	204	12.3	138	46.3	156	13.1
217	10.4	177	64.6	217	11.4	147	22.5	158	12.8
233	39.5	178	27.0	233	33.0	153	59.1	174	77.4
423	11.6	183	24.8	304	13.1	165	23.8	290	99.8
537	11.3	191	24.5	376	35.4	174	14.3	291	78.3
		195	100.0	377	10.2	183	62.3	292	12.3
		196	20.4	381	17.9	195	13.3	304	100.0
		203	50.8	423	18.2	290	80.3	305	59.5
		233	22.8	537	11.8	291	17.5	306	23.4
		279	10.7			304	100.0		
		281	10.4			305	24.9		
		283	10.9			381	12.8		
		290	43.1			423	18.2		
		304	47.0						
		381	62.6						
		382	19.7						
		383	17.3						
		395	23.6						
		397	19.7						
		407	13.0						
		409	19.3						
		423	70.4						
		424	24.0						
		425	32.5						
		426	10.1						

Table S-4: Positive-ion mode DART-MS measurements for nominal masses with relative abundances above a 10% threshold for *D. ceratocaula* extracts prepared using the indicated solvents. The corresponding spectra appear in Supplementary Information Figure S-4.

Hexane		**Ethyl acetate**		**Dichloromethane**		**Ethanol**		**Water**	
m/z	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**
71	16.9	86	35.8	85	13.8	86	44.6	85	27.4
85	28.1	89	100.0	86	26.7	93	44.5	86	50.5
99	10.4	90	34.0	113	10.3	94	14.3	87	13.5
163	37.4	106	10.7	163	38.0	130	18.0	89	25.9
191	30.8	163	19.4	191	27.6	171	15.2	90	14.5
195	60.3	177	32.5	195	100.0	259	18.5	97	13.0
196	18.1	178	10.5	196	21.4	371	100.0	99	10.5
203	49.6	191	13.4	203	47.0	372	78.3	104	44.4
233	38.8	195	51.9	233	28.5	373	16.7	116	34.3
263	16.0	196	10.4	257	10.3	388	16.1	118	10.3
281	45.8	203	23.5	263	12.0			120	12.7
283	22.0	233	10.6	281	42.5			124	10.8
298	10.7	257	10.4	283	27.3			127	34.6
381	41.4	281	42.3	376	13.7			129	27.4
382	13.4	283	23.7	381	12.5			130	51.7
395	12.8	298	16.7	395	16.9			132	17.3
423	16.6	381	21.1	423	24.0			133	43.6
509	11.5	423	37.6	663	19.5			142	17.6
537	34.8	424	16.1					145	29.6
538	14.2	425	11.2					146	61.2
565	12.1							147	25.5
576	24.5							148	15.1
577	10.1							158	26.1
578	13.5							163	12.4
593	16.7							165	25.5
600	27.4							172	14.2
601	11.4							174	100.0
602	18.2							175	35.3
604	11.4							179	18.1
618	12.2							180	12.5
647	34.0							183	74.0
648	15.8							290	26.1
663	100.0							371	14.5
664	47.7							381	10.4
665	11.9								

Table S-5: Positive-ion mode DART-MS measurements for nominal masses with relative abundances above a 10% threshold for *D. discolor* extracts prepared using the indicated solvents. The corresponding spectra appear in Supplementary Information Figure S-5.

Hexane		**Ethyl acetate**		**Dichloromethane**		**Ethanol**		**Water**	
m/z	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**
85	13.8	89	80.5	89	27.4	86	16.3	73	12.4
163	19.3	90	41.5	109	10.0	93	100.0	85	41.7
191	18.9	106	15.1	113	23.7	94	16.4	86	46.6
195	26.9	163	44.7	127	16.9	195	32.5	93	25.4
203	25.1	177	42.3	145	10.8	255	14.5	97	22.0
233	23.2	178	15.9	156	17.4	257	19.0	104	48.5
509	10.6	191	24.7	157	10.5	259	20.8	116	67.0
537	33.3	195	100.0	163	39.4	263	11.9	118	15.0
538	13.7	196	38.5	164	11.3	281	47.4	127	100.0
565	11.5	203	47.2	191	35.8	282	10.3	129	18.7
593	15.3	233	17.6	195	100.0	283	40.1	130	19.5
600	29.3			196	22.7	285	12.3	130	34.3
601	12.2			203	43.4	381	12.6	132	23.5
647	46.2			233	24.8	407	10.7	145	93.6
648	21.6			371	15.0	423	20.0	146	15.8
663	100.0					425	15.4	147	22.0
664	47.2							156	14.0
665	11.8							163	33.2
								165	22.8
								169	15.7
								174	92.0
								180	24.5
								183	53.6
								198	15.4
								209	43.7
								255	11.1
								257	17.9
								263	14.3
								281	48.3
								282	13.8
								283	11.2
								283	55.4
								284	10.8
								329	12.1
								355	11.4
								357	11.9
								371	84.4
								372	25.6
								381	10.6
								388	12.4

Table S-6: Positive-ion mode DART-MS measurements for nominal masses with relative abundances above a 10% threshold for *D. ferox* extracts prepared using the indicated solvents. The corresponding spectra appear in Supplementary Information Figure S-6.

Hexane		**Ethyl acetate**		**Dichloromethane**		**Ethanol**		**Water**	
m/z	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**
71	22.6	89	29.8	71	12.5	93	31.7	86	47.3
85	22.9	106	16.9	85	17.6	135	10.7	90	16.8
99	13.5	177	100.0	109	10.8	142	14.6	93	24.3
113	14.2	178	21.4	111	12.0	174	23.2	100	16.6
156	14.0	195	12.1	113	19.0	195	14.6	104	36.1
163	56.4	203	11.7	127	10.1	257	22.0	110	31.6
191	57.0	281	21.8	135	13.7	263	14.1	116	54.7
192	10.8	283	17.4	156	13.7	279	10.4	117	10.1
195	100.0	338	38.0	163	71.5	281	53.9	118	28.1
196	27.6	339	10.7	164	13.1	282	11.1	127	16.2
202	10.4	381	27.5	191	59.9	283	59.0	130	30.4
203	91.2	395	10.2	192	10.1	284	11.6	132	4.02
204	19.6	409	11.3	195	100.0	285	11.9	135	63.4
217	23.2	423	43.6	196	34.2	298	21.7	138	14.3
233	79.4	424	14.4	203	85.9	300	13.3	142	100.0
234	17.7	425	12.4	204	17.4	304	11.1	143	17.3
247	14.8			217	19.2	338	32.9	145	19.5
259	10.9			233	59.8	339	10.8	152	50.5
281	12.0			234	10.5	371	11.0	156	13.3
283	11.1			257	14.5	381	43.8	158	58.0
298	10.0			259	10.7	382	13.8	163	31.6
338	10.8			281	33.8	383	15.0	163	66.6
423	10.2			283	32.0	395	28.9	174	59.4
663	16.3			284	11.6	397	23.8	180	56.8
				298	13.1	407	11.0	180	26.8
				338	18.8	409	32.7	198	49.3
				371	17.2	410	10.6	209	16.8
				371	19.1	423	100.0	223	22.1
				376	27.9	424	33.1	224	23.6
				381	40.4	425	28.9	304	82.8
				382	12.8	576	27.0	305	28.8
				395	31.9	577	11.3	371	58.3
				409	13.9	578	26.0	372	14.7
				423	30.5	600	14.3	388	22.5
				424	10.2	602	28.7		
				537	20.5	603	12.0		
				576	18.9	604	24.2		
				578	13.5	618	10.6		
				593	11.0				
				600	15.3				
				602	18.0				
				604	12.5				
				618	10.3				
				647	14.2				
				663	58.3				

Table S-7: Positive-ion mode DART- measurements for nominal masses with relative abundances above a 10% threshold for *D. inoxia* extracts prepared using the indicated solvents. The corresponding spectra appear in Supplementary Information Figure S-7.

Hexane		**Ethyl acetate**		**Dichloromethane**		**Ethanol**		**Water**	
m/z	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**
71	15.8	89	100.0	89	34.8	85	69.4	85	25.9
85	23.4	90	36.1	114	14.2	90	28.5	90	24.9
163	14.5	106	20.6	119	10.7	93	13.1	97	10.6
191	18.2	127	13.8	135	32.5	97	43.9	104	27.0
195	44.8	145	15.9	163	48.3	99	16.1	116	19.2
203	37.9	163	16.7	191	36.5	116	100.0	118	19.8
233	38.6	163	25.3	195	100.0	118	21.5	127	49.6
259	17.0	177	45.2	196	22.1	120	13.0	132	15.3
284	12.3	178	11.2	203	70.1	127	97.0	133	13.3
371	12.6	180	26.0	204	11.6	128	10.3	138	52.5
423	13.8	191	13.7	217	13.6	145	98.2	142	42.7
509	11.5	195	52.2	233	43.1	146	11.6	145	55.4
537	39.2	196	13.0	371	30.1	158	10.6	146	14.0
538	15.7	198	14.6	372	11.0	162	13.6	158	18.8
565	15.3	203	24.2			163	89.2	163	36.0
593	22.9	233	12.5			166	13.2	174	80.6
594	10.4	259	13.7			174	12.1	175	11.4
600	29.1	283	16.4			180	89.2	180	47.2
601	12.3	304	17.5			198	42.5	198	25.1
604	10.0	371	42.0			229	13.6	304	100.0
647	44.7	372	10.4			247	23.1	305	31.4
648	20.8	381	29.8			253	13.6	325	14.7
663	100.0	395	14.0			259	15.5	371	79.5
664	48.7	397	18.5			271	32.8	372	29.7
665	12.1	407	14.9			289	61.9	373	18.8
		409	19.8			304	38.4		
		423	84.5			307	13.7		
		424	28.7			325	45.7		
		425	38.8			342	10.0		
		426	12.2			371	60.1		
		441	13.9			372	16.6		
		576	10.5			381	11.0		
		578	15.4			414	10.4		
		602	15.6			423	13.7		
		604	16.6			440	19.1		
		663	10.0			486	20.2		

Table S-8: Positive-ion mode DART-MS measurements for nominal masses with relative abundances above a 10% threshold for *D. leichhardtii* extracts prepared using the indicated solvents. The corresponding spectra appear in Supplementary Information Figure S-8.

Hexane		**Ethyl acetate**		**Dichloromethane**		**Ethanol**		**Water**	
m/z	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**
71	11.0	61	10.2	69	18.9	93	100.0	121	11.8
163	34.1	89	100.0	71	50.8	142	18.6	124	28.6
191	28.5	177	13.5	73	12.9	149	19.2	142	`100.0
195	100.0	281	10.6	83	51.7	163	17.2	143	16.0
196	13.0	283	33.1	85	54.2	174	14.4	174	23.4
203	44.0			89	11.5	279	13.3	290	34.7
233	51.8			91	16.3	281	16.7	371	15.8
281	10.8			95	18.0	283	34.7		
283	24.4			97	19.1	290	17.4		
371	14.0			101	12.6	295	13.4		
509	10.3			109	19.1	297	15.1		
531	14.7			111	21.9	371	26.5		
537	25.7			113	20.3	445	13.0		
538	10.1			114	24.7	531	15.7		
600	29.8			123	10.3	578	10.4		
601	11.7			125	11.9				
647	25.8			127	12.3				
648	11.3			135	10.0				
663	84.5			137	10.7				
664	39.1			149	11.0				
				155	17.1				
				156	13.2				
				157	15.1				
				161	10.5				
				163	56.0				
				164	10.0				
				179	12.4				
				191	38.5				
				195	100.0				
				196	16.3				
				203	48.5				
				233	38.3				
				239	19.3				
				257	27.8				
				265	11.4				
				279	15.1				
				281	33.0				
				283	62.5				
				284	13.3				
				295	16.7				
				297	26.4				
				313	12.3				
				371	23.8				
				376	46.4				
				377	11.3				
				381	10.4				
				393	26.4				

				411	11.1				
				467	13.4				
				509	10.2				
				537	31.1				
				538	12.6				
				552	15.0				
				576	14.5				
				578	36.0				
				579	13.6				
				593	12.6				
				600	48.6				
				601	20.2				
				602	12.8				
				604	13.5				
				663	99.3				
				664	44.8				

Table S-9: Positive-ion mode DART-MS measurements for nominal masses with relative abundances above a 10% threshold for *D. quercifolia* extracts prepared using the indicated solvents. The corresponding spectra appear in Supplementary Information Figure S-9.

Hexane		**Ethyl acetate**		**Dichloromethane**		**Ethanol**		**Water**	
m/z	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**
163	33.5	89	100.0	71	24.8	93	100.0	124	58.5
191	31.5	90	13.4	83	24.1	124	49.0	142	56.5
195	100.0	163	14.6	85	11.5	195	10.6	156	29.2
196	14.0	177	42.2	113	20.6	281	11.7	172	33.4
203	42.6	191	10.7	127	14.9	290	70.4	174	43.2
233	39.5	195	42.3	163	63.3	291	14.2	290	100.0
663	13.7	203	13.5	164	10.1	445	10.9	291	26.4
		233	13.4	191	56.7	531	12.6	304	14.9
		281	16.6	195	100.0				
		291	10.2	196	18.0				
		423	14.5	203	80.1				
		531	71.0	204	13.4				
		532	25.2	217	13.9				
		576	11.5	233	64.7				
				234	10.9				
				338	18.2				
				395	11.3				

Table S-10: Positive-ion mode DART-MS measurements for nominal masses with relative abundances above a 10% threshold for *D. stramonium* extracts prepared using the indicated solvents. The corresponding spectra appear in Supplementary Information Figure S-10.

Hexane		**Ethyl acetate**		**Dichloromethane**		**Ethanol**		**Water**	
m/z	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**
163	27.2	89	100.0	113	11.9	89	20.7	124	59.2
191	25.2	90	24.7	163	63.0	93	42.4	135	19.4
195	100.0	106	17.1	191	48.7	101	10.6	174	20.9
196	16.5	177	32.4	195	100.0	114	17.0	290	92.9
203	35.4	195	17.6	196	24.7	115	10.9	291	32.8
233	25.0			203	80.1	119	14.2	304	15.5
				204	14.9	124	100.0	371	100.0
				217	15.6	135	49.6	372	37.8
				233	55.4	147	10.9	373	24.5
				234	10.7	152	10.2	388	17.7
				376	21.7	195	31.7		
				381	15.0	241	10.0		
				395	12.0	257	24.7		
				537	14.6	259	29.2		
				600	11.6	285	14.4		
				647	19.3	290	92.9		
				663	48.7	291	17.8		
				664	22.7	371	63.0		
						372	23.1		
						373	14.8		
						381	14.6		
						388	11.0		
						423	14.4		

Table S-11: Positive-ion mode DART-MS measurements for nominal masses with relative abundances above a 10% threshold for *D. wrightii* extracts prepared using the indicated solvents. The corresponding spectra appear in Supplementary Information Figure S-11.

Hexane		**Ethyl acetate**		**Dichloromethane**		**Ethanol**		**Water**	
m/z	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**	***m/z***	**Rel. Int.**
71	16.4	95	13.7	71	11.0	86	54.9	86	31.3
85	25.3	113	10.6	85	12.6	93	90.8	104	12.4
163	54.8	124	10.7	99	37.5	94	18.9	116	12.3
191	47.1	163	28.5	113	22.9	99	21.6	118	14.1
195	100.0	191	17.1	117	31.3	110	24.6	124	46.9
196	30.9	195	100.0	135	15.1	117	14.1	130	44.9
203	63.0	196	23.6	147	14.9	123	11.4	132	15.8
204	13.6	203	41.3	153	87.6	124	65.8	138	16.5
217	15.5	233	15.9	163	59.0	127	18.6	142	70.6
233	50.3	255	13.8	165	15.5	130	69.4	143	10.1
234	11.2	257	37.2	183	33.3	138	10.0	146	21.9
281	30.8	259	17.0	191	37.9	142	13.8	158	44.2
283	40.7	263	16.7	195	100.0	145	13.2	171	10.6
284	10.3	279	14.8	196	27.7	147	17.4	174	96.0
381	21.6	281	73.7	203	54.4	153	100.0	175	16.1
397	12.6	282	14.9	233	24.6	165	19.6	183	14.5
537	22.3	283	91.8	263	14.3	170	20.9	276	29.1
593	12.6	284	19.3	281	56.6	174	18.8	290	100.0
600	18.4	285	17.1	282	11.4	183	62.2	291	67.1
647	22.3	298	18.5	283	40.1	190	10.4	292	11.1
648	10.3	300	13.8	298	11.6	195	17.6	304	84.7
663	62.3	381	61.8	371	20.5	257	21.1	305	20.8
664	28.5	382	19.3	376	20.1	263	12.7	306	33.7
		383	22.3	395	11.3	276	21.4		
		395	22.0	397	10.7	279	20.1		
		397	31.6	537	14.8	281	64.3		
		398	10.0	600	11.6	282	12.7		
		409	15.9	647	12.1	283	52.5		
		423	28.6	663	46.4	290	66.9		
		425	20.6	664	21.3	291	13.9		
		576	24.2			298	16.7		
		577	10.0			304	27.9		
		578	15.9			381	30.4		
		600	16.1			383	12.4		
		602	19.0			395	10.2		
		604	12.0						

Table S-12: Relative abundances for peaks at the indicated nominal *m/z* values in the extract comprised of ethyl acetate/ethanol/water. Unless otherwise indicated, listed peaks are those whose abundance is above a 10% threshold.[a,b] The corresponding spectra appear in Supplementary Information Figure S-12.

m/z	*D. ceratocaula*	*D. discolor*	*D. ferox*	*D. inoxia*	*D. leichhardtii*	*D. metel*	*D. quercifolia*	*D. stramonium*	*D. wrightii*
85		17.3		13.0					
86	64.2	25.1							21.9
90	10.1			15.1		13.8			13.7
93	79.2	27.2	53.1	32.4	45.4	38.6	43.6	66.2	27.7
94	11.0		15.3					16.5	
97		13.0							
104	38.5	12.0	10.0						
110									13.2
112			12.5						
116	11.2	29.9	13.5	24.8		29.7			
118									13.6
124	65.2				70.7	69.6	91.8	94.7	60.6
125							10.5	26.8	
127	10.0	32.0	12.9	22.3					
130	53.5	17.9	12.9						32.2
133			15.2	23.9					26.6
138			50.0	52.7		56.0	17.8	22.5	19.6
140	7.2		3.9	2.2	2.6	2.6	2.9	3.1	3.0
142	27.9	4.0	64.3	29.1	96.5	3.9	20.5	11.3	45.2
143					15.2				
145		30.3	12.9	25.1					
146			10.4	21.9	14.7				17.4
147		12.6							
156	7.1	14.3	9.8	10.2	2.7	7.8	14.4	2.5	5.9
158	8.5	8.0	75.2	26.6	13.8	15.3	2.7	6.7	30.9
160			60.8						
163		15.6							
165		17.7							
171	41.0								
174	58.9	64.6	97.5	79.1	59.9	53.4	22.4	26.3	78.3
175			14.2	15.0					10.0
177			91.9					14.3	14.0
178			16.5						
180		19.9		17.8					
183	11.8	48.1							
185			10.2						
189			10.1						
193	77.5								
194		15.2							
198		12.3		11.1					
201								25.4	
209		100.0	55.7						
210		15.0							
215				15.8					10.5
223			25.3						

241								68.1	
242								22.3	
243								39.7	
257	10.6								
276				13.6					46.4
278	10.8								
283	13.4								
290	100.0	2.2	6.0	11.9	100.0	100.0	100.0	100.0	100.0
291	35.6				37.7	59.2	41.2	57.8	71.7
292						86.6	25.3	23.0	12.9
304	6.6	25.0	100.0	100.0	2.5	36.1	31.4	17.0	70.6
305			37.4	48.4		19.0			23.3
306			12.0	28.8					39.6
314	24.2		41.3						
353			23.8						
383	26.5								
387			18.0						
485								12.6	
490			17.1						
563			10.0						

[a]Peaks at *m/z* values of 138, 140, 142, 156, 158, 174, 290, and 304 represent tyramine, tropinone, tropine, scopoline, dihydroxytropane, trihydroxytropane, atropine/hyoscyamine, and scopolamine/hyoscine respectively, as determined through comparison of the in-source CID data of authentic standards with the in-source CID seed spectra recorded under identical conditions.

[b]Peaks at *m/z* 138, 140, 142, 156, 158, 174, 290, and 304 represent diagnostic alkaloids that were observed above a 2% threshold.

Table S-13: Feature masses derived from *Datura* spp. seed DART-MS spectra that were used to construct the linear discriminant analysis (LDA) plot in Figure 4.

m/z	***m/z***	***m/z***
74.081	163.072	304.152
86.059	171.122	338.323
90.103	174.110	358.358
110.064	174.111	398.355
130.049	190.135	415.357
136.057	193.047	423.357
138.105	209.041	425.362
142.122	282.274	441.387
144.100	283.243	445.205
145.048	290.172	460.431
153.084	291.172	507.495
158.115	300.273	-

Table S-14: Relative standard deviation (RSD) values for eight diagnostic alkaloid peaks observed in the averaged spectra of the indicated *Datura* species.

m/z[a]	*D. ceratocaula*	*D. discolor*	*D. ferox*	*D. inoxia*	*D. leichhardtii*	*D. metel*	*D. quercifolia*	*D. stramonium*	*D. wrightii*	Median	Range
138	30.40	12.90	49.33	86.13	33.92	33.19	41.59	76.86	39.95	39.95	73.23
140	13.50	29.76	49.08	125.46	18.01	28.44	49.59	46.82	59.54	46.82	111.96
142	61.59	37.31	14.61	76.98	23.16	15.06	33.52	38.37	59.85	37.31	62.37
156	26.48	31.98	24.79	64.24	19.90	15.61	34.09	22.10	23.95	24.79	48.63
158	47.87	57.59	22.63	55.17	28.42	14.82	47.47	53.14	39.55	47.47	42.77
174	12.53	0.00	18.30	11.47	7.82	30.15	33.27	31.21	17.88	17.88	33.27
290	73.01	-	-	42.30	5.84	6.64	10.27	12.86	63.52	12.86	67.17
304	59.25	50.04	41.51	19.96	38.73	6.98	35.93	68.85	33.29	38.73	61.87

[a]Peaks at the nominal *m/z* values of 138, 140, 142, 156, 158, 174, 290, and 304 represent tyramine, tropinone, tropine, scopoline, dihydroxytropane, trihydroxytropane, atropine/hyoscyamine, and scopolamine/hyoscine respectively, as determined through comparison of the in-source CID data of authentic standards with the in-source CID seed spectra recorded under identical conditions.