Electronic Supplementary Material (ESI) for Analytical Methods.

In situ analysis of *Asimina triloba* (paw paw) plant tissues for acetogenins via the droplet–liquid microjunction surface sampling probe coupled to UHPLC–PDA–HRMS/MS

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Supporting Information

Figure S1. The structure, the ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), HRMS and MS/MS spectra for annonacin.

Figure S2. Plots of *m/z* 603.4807±100 Da with a mass defect of ±25 mDa.

Figure S3. The leaves and flowers as they were prepared for cryotome cross-sectioning.

Table S1. The populated list using mass defect filtering for ±100 Da with a mass defect of ±25 mDa around *m/z* 603.4807 for a seed, pulp, twig, ovary, leaf, and petal from an *Asimina triloba* tree.

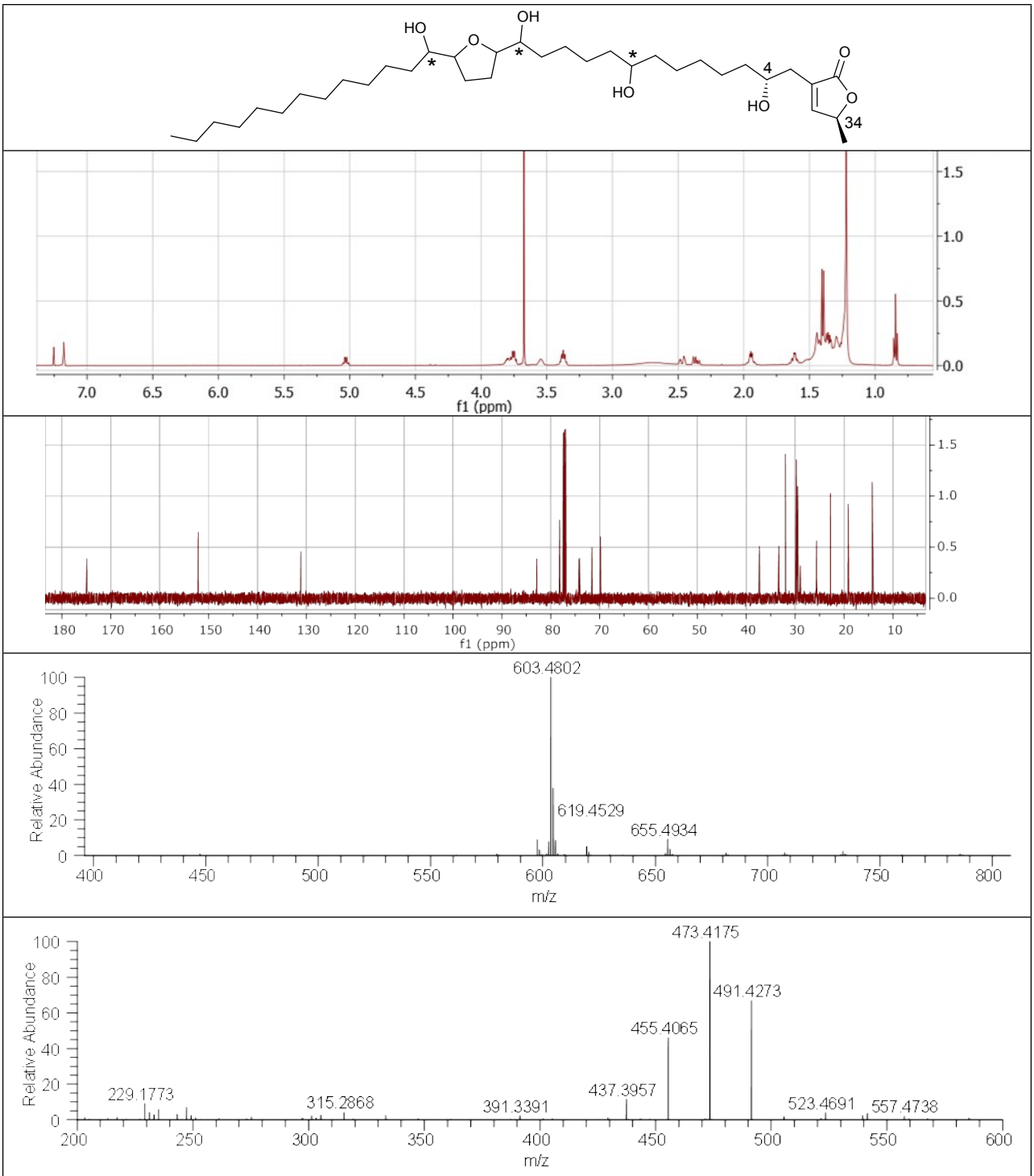

Figure S1. The structure, the ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), HRMS and MS/MS spectra for annonacin. The stereocenters were determined by preparing Mosher ester derivatives and the compound was identified as annonacin.[51]

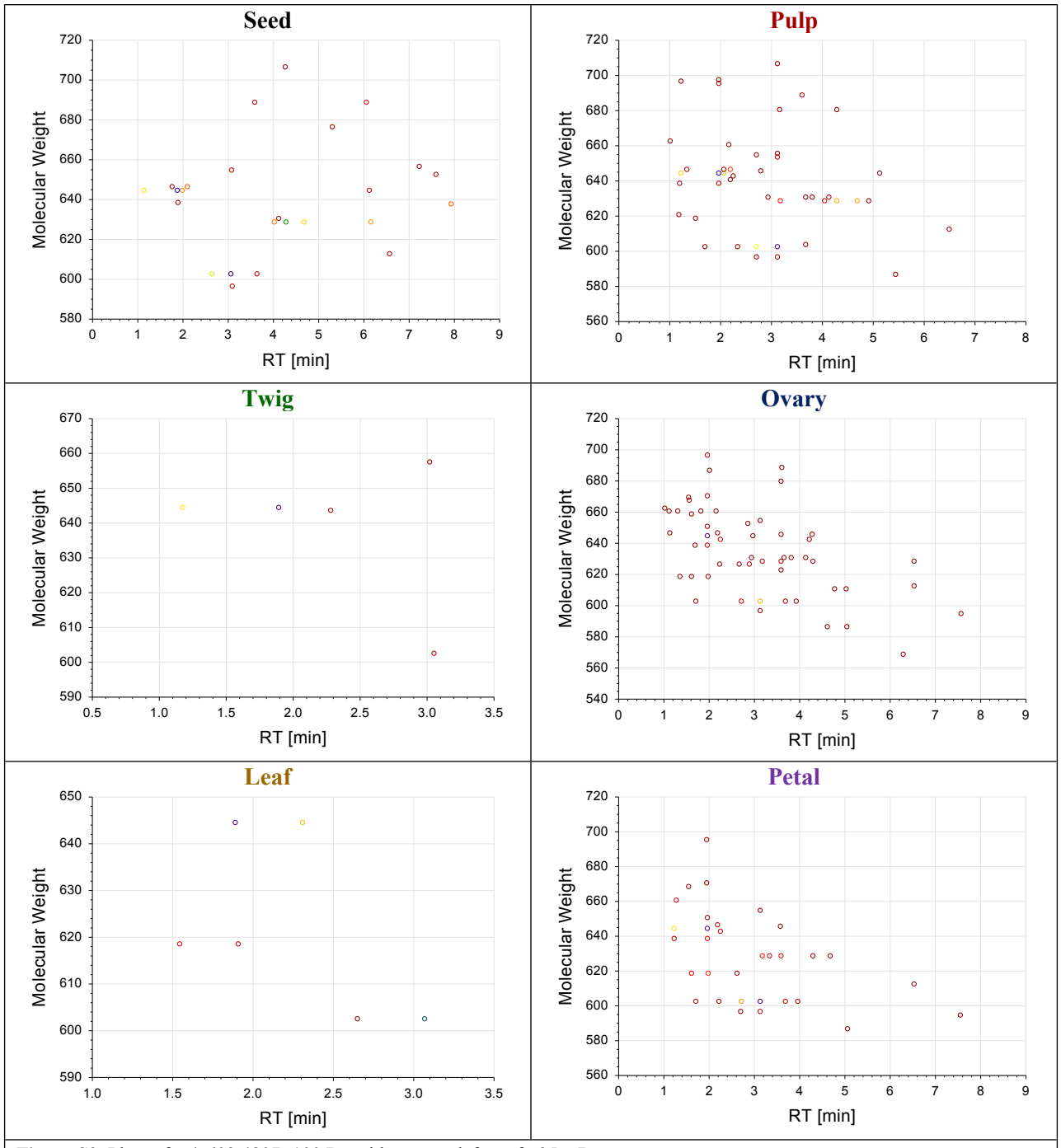

Figure S2. Plots of *m/z* 603.4807±100 Da with a mass defect of ±25 mDa.

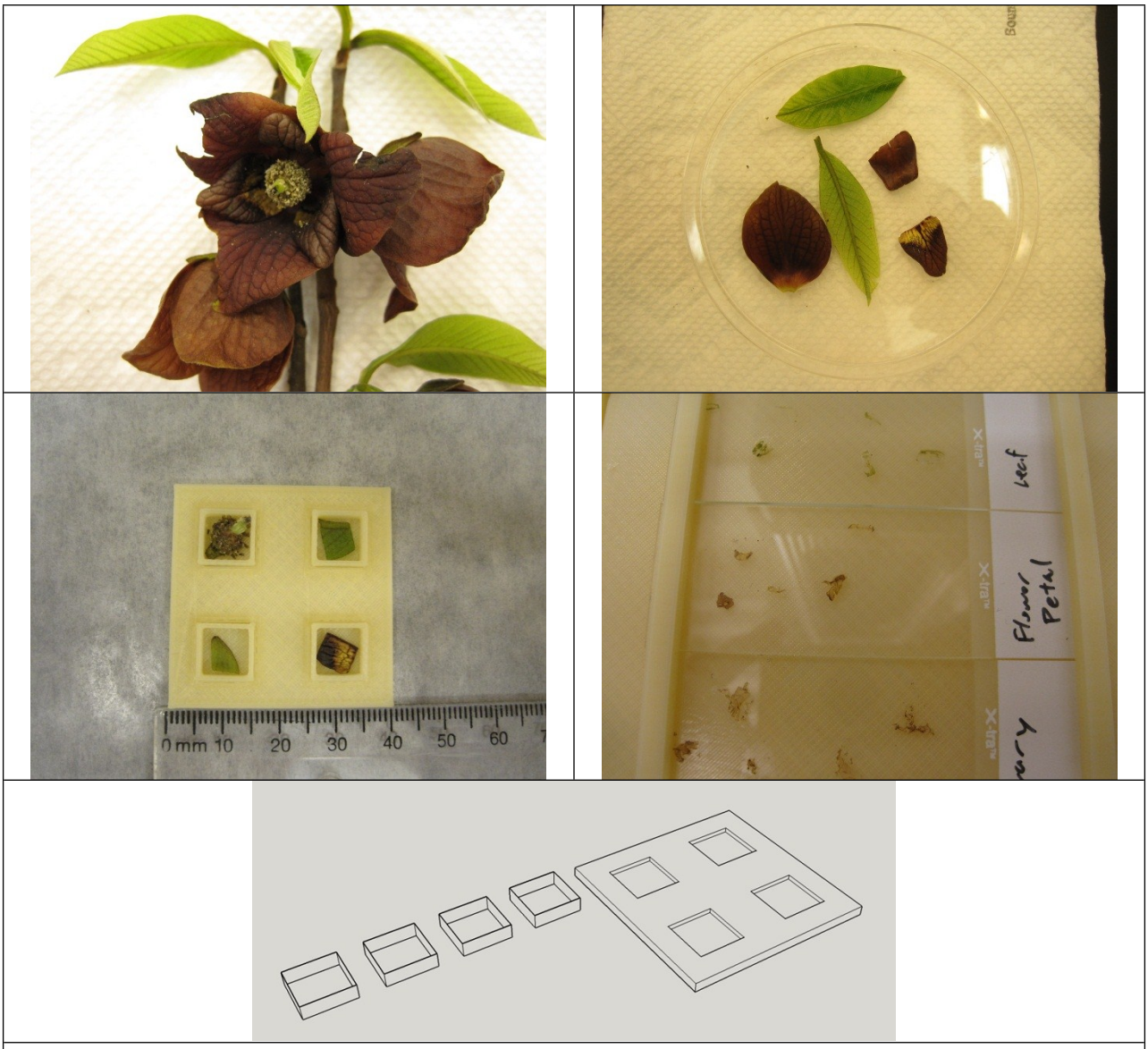

Figure S3. The leaves and flowers of *Asimina triloba* as they were prepared for cryotome cross-sectioning. A 3D printed tray was created for the application of the optimum cutting temperature (O.C.T.) embedding medium prior to cross-sectioning. This tray was created using SketchUp Make and printed on an F306 3D printer.

Table S1. The populated list using mass defect filtering for ±100 Da with a mass defect of ±25 mDa around *m/z* 603.4807 for a seed, pulp, twig, ovary, leaf, and petal from an *Asimina triloba* tree.

Retention Time (min)	$[M + Li]^+$					
	Seed	Pulp	Twig	Ovary	Leaf	Petal
1.02		663.5031		663.5035		
1.12				661.4886		
1.15				647.5056		
1.20		621.4915				
1.23	645.4911	645.4913	645.4930			645.4927
1.25		697.5055				
1.30				661.4882		661.4875
1.37		647.5084		619.4775		
1.53		619.4758				
1.56						669.4760
1.61				619.4770	619.4779	619.4775
1.63				659.4738		
1.70				639.4852		
1.71		603.4822		603.4823		603.4822
1.83		647.5071		661.4876		
1.96	645.4911				645.4932	
1.97		671.5073				671.5078
1.97				651.4984		651.5001
1.98				697.5064		
1.99		645.4913	645.4925	619.4774	619.4778	619.4775
2.02				687.5037		
2.08	645.4911	645.4913				
2.09		647.5008				
2.17		661.4863		661.4871		
2.19	647.5079	647.5071		647.5084		647.5084
2.22						603.4827
2.25				627.4820		
2.27		643.4758		643.4770		643.4774
2.36		603.4810				
2.38					645.4932	
2.63						619.4789
2.68				627.4820		
2.72	603.4811	603.4810		603.4822	603.4838	603.4827
2.73		655.4949				
2.87				653.4797		
2.89				627.4820		
2.96		631.5076		631.5119		
2.98				645.4932		
3.13						655.4960
3.14	603.4810	603.4810	603.4837	603.4822	603.4825	603.4824
3.15	655.4946			655.4958		
3.18		681.5083				
3.19		629.4965		629.4979		629.4981
3.34						629.4981
3.59				629.4979		629.4981
3.64	689.5172	689.5174		689.5189		
3.67		631.5122		631.5106		
3.70	603.4829			603.4823		603.4825
3.82		631.5126		631.5107		
3.95				603.4826		603.4819
4.08	629.4961	629.4965				
4.17	631.5119	631.5121		631.5137		
4.22				643.4773		
4.31	629.4961	629.4965		629.4979		629.4981
4.32				681.5095		

4.62				**587.4877**		
4.70	**629.4961**	**629.4965**				**629.4981**
4.78				**611.4872**		
4.94		**629.4965**				
5.04				**611.4866**		
5.06				**587.4874**		**587.4880**
5.14		**645.4917**				
5.38	**677.4804**					
5.47		**587.4858**				
6.14	**689.5173**					
6.20	**645.4901**					
6.23	**629.5170**					
6.29				**569.4768**		
6.52		**613.5013**		**613.5026**		**613.5027**
6.54				**629.4770**		
6.64	**613.5018**					
7.31	**657.5126**					
7.57				**595.4928**		**595.4942**
7.68	**653.4917**					