

Supporting Information for
Quantification of Toxins in Soapberry Fruit (*Sapindaceae*): Hypoglycin A and
Methylenecyclopropylglycine

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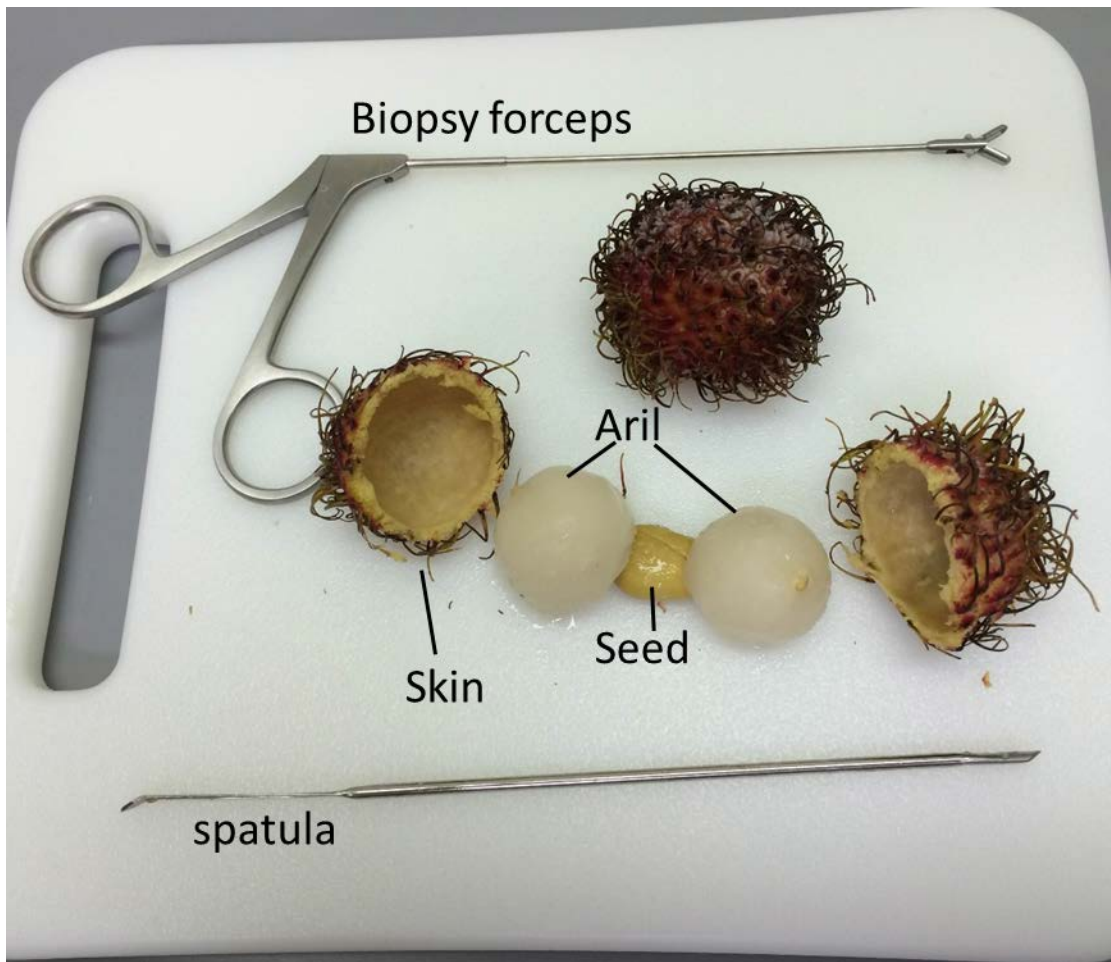


Figure S1. Photograph of rambutan dissection for method matrix blank preparation, including labels of each fruit component and tools for sampling.

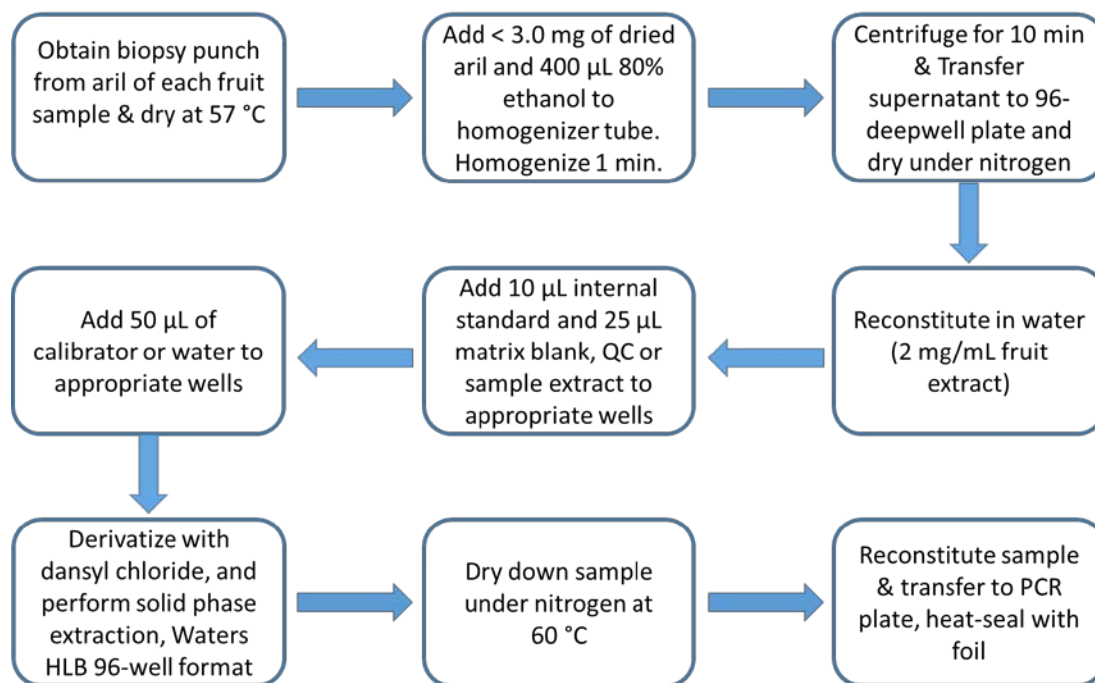


Figure S2. Analytical flowchart for soapberry fruit extraction, derivatization and analysis by HPLC-MS/MS.

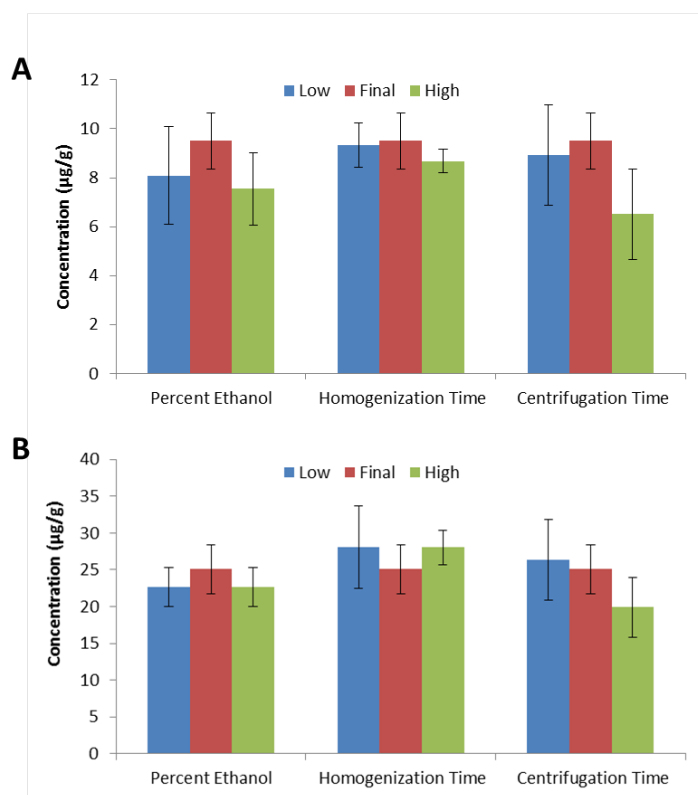


Figure S3. Litchi extraction ruggedness testing where percent ethanol was varied from 60% (low), 80% (final), and 100% (high), homogenization time was varied from 30 seconds (low), 1 minute (final), and 90 seconds (high), and centrifugation time was varied from 5 minutes (low), 10 minutes (final), and 15 minutes (high) for (A) MCPG and (B) HGA.

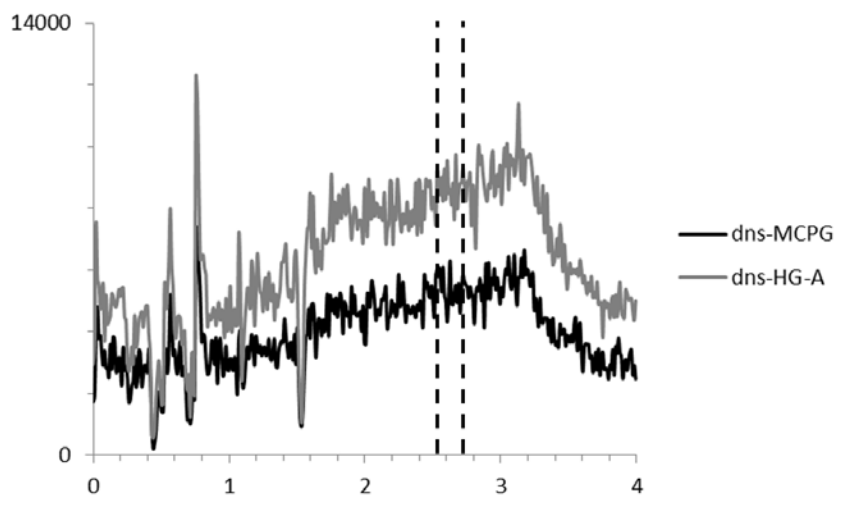


Figure S4. Evaluation of matrix effects. A 5.0 μL injection of 1.00 mg/mL rambutan extract in 0.1% formic acid in water was injected while infusing 100. ng/mL HGA (gray) and MCPG (black). Matrix effects were not observed at the expected elution time (dashed vertical lines) of either analyte (2.72 min for dns-HGA and 2.56 min for dns-MCPG) in the extracted ion chromatogram for the transitions m/z 375.1 \rightarrow 170.1 and m/z 361.1 \rightarrow 170.1, respectively.

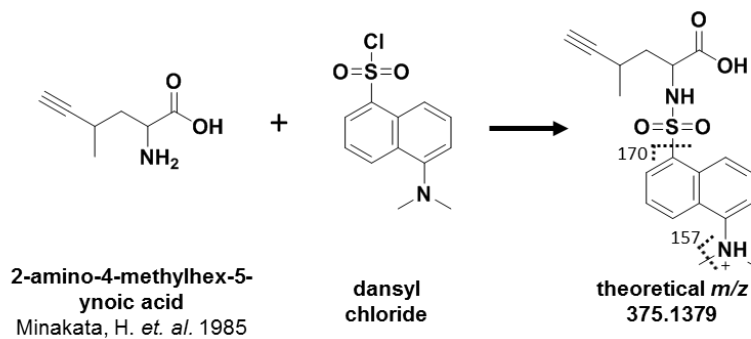
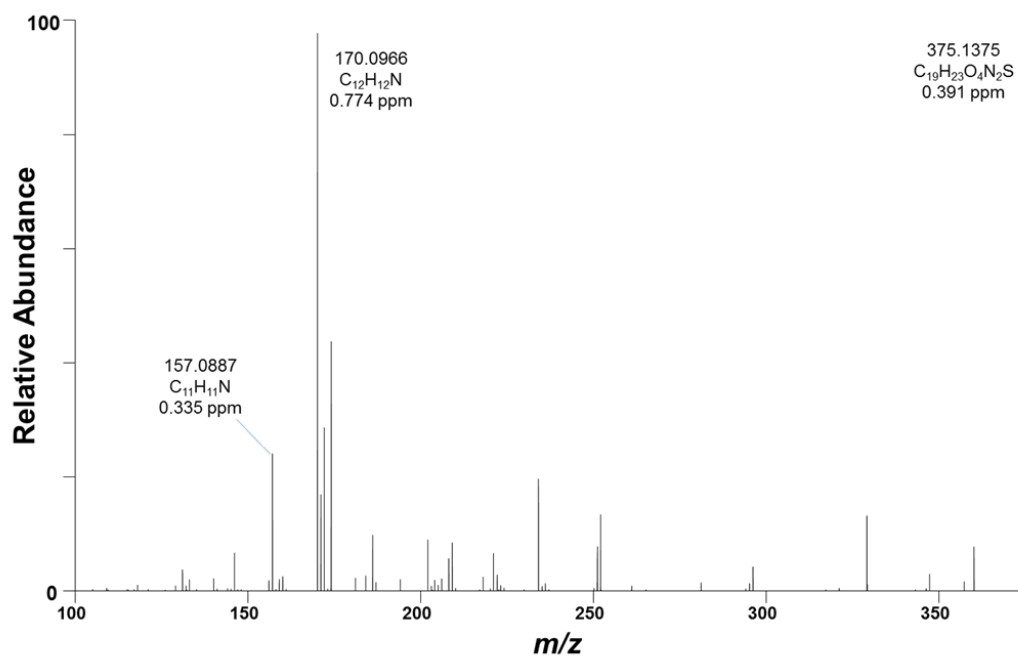
A**B**

Figure S5. High mass accuracy identification of 2-amino-4-methylhex-5-ynoic acid in longan aril, as previously reported in longan seeds by H. Minakata, *et. al.* (A) Derivatization with dansyl chloride and theoretical exact mass (B) product ion mass spectra of m/z 375.1373 (experimental m/z 375.1375, 0.391 ppm error).

Table S1. SPE recovery for both analytes at three concentrations (n=3).

Analyte	Standard	Peak Areas with SPE	Peak Areas without SPE	% Recovery
MCPG	S1 (1.00 ng/mL)	$(1.56 \pm 0.27) \times 10^3$	$(2.20 \pm 0.20) \times 10^3$	71 ± 14
	S5 (20.0 ng/mL)	$(3.43 \pm 0.39) \times 10^4$	$(5.34 \pm 0.30) \times 10^4$	64 ± 8
	S8 (200 ng/mL)	$(2.71 \pm 0.25) \times 10^5$	$(5.09 \pm 0.24) \times 10^5$	53 ± 5
HGA	S1 (1.00 ng/mL)	$(3.39 \pm 0.41) \times 10^3$	$(4.45 \pm 0.50) \times 10^3$	76 ± 13
	S5 (20.0 ng/mL)	$(6.76 \pm 0.81) \times 10^4$	$(9.17 \pm 0.54) \times 10^4$	74 ± 10
	S8 (200 ng/mL)	$(5.09 \pm 0.27) \times 10^5$	$(8.06 \pm 0.37) \times 10^5$	63 ± 4

Table S2. Accuracy and precision of dilution experiments to extend dynamic range for MCPG, where 1, 5, and 10 mg/g (MCPG/dried fruit) samples were diluted 50:1 with water prior to derivatization.

mg/g fruit	ng/mL			mg/g fruit			ave	stdev	% Error	% RSD
1	20.8	18.2	22.3	1.04	0.910	1.12	1.02	0.10	2.2	10
5	91.9	98.0	96.4	4.60	4.90	4.82	4.77	0.16	-4.6	3.3
10	204	194	217	10.2	9.70	10.9	10.3	0.60	2.5	5.6

Table S3. Accuracy and precision of dilution experiments to extend dynamic range for HGA, where 1, 5, and 10 mg/g (HGA/dried fruit) samples were diluted 50:1 with water prior to derivatization.

mg/g fruit	ng/mL			mg/g fruit			ave	stdev	% Error	% RSD
1	22.3	19.2	24.3	1.12	0.960	1.22	1.10	0.13	9.7	12
5	103	98.8	106	5.15	4.94	5.30	5.13	0.18	2.6	3.5
10	193	195	224	9.65	9.75	11.2	10.2	0.90.	2.0	8.5