Supporting Information

Distinguishing Malignant from Benign Microscopic Skin Lesions Using Desorption Electrospray Ionization Mass Spectrometry Imaging

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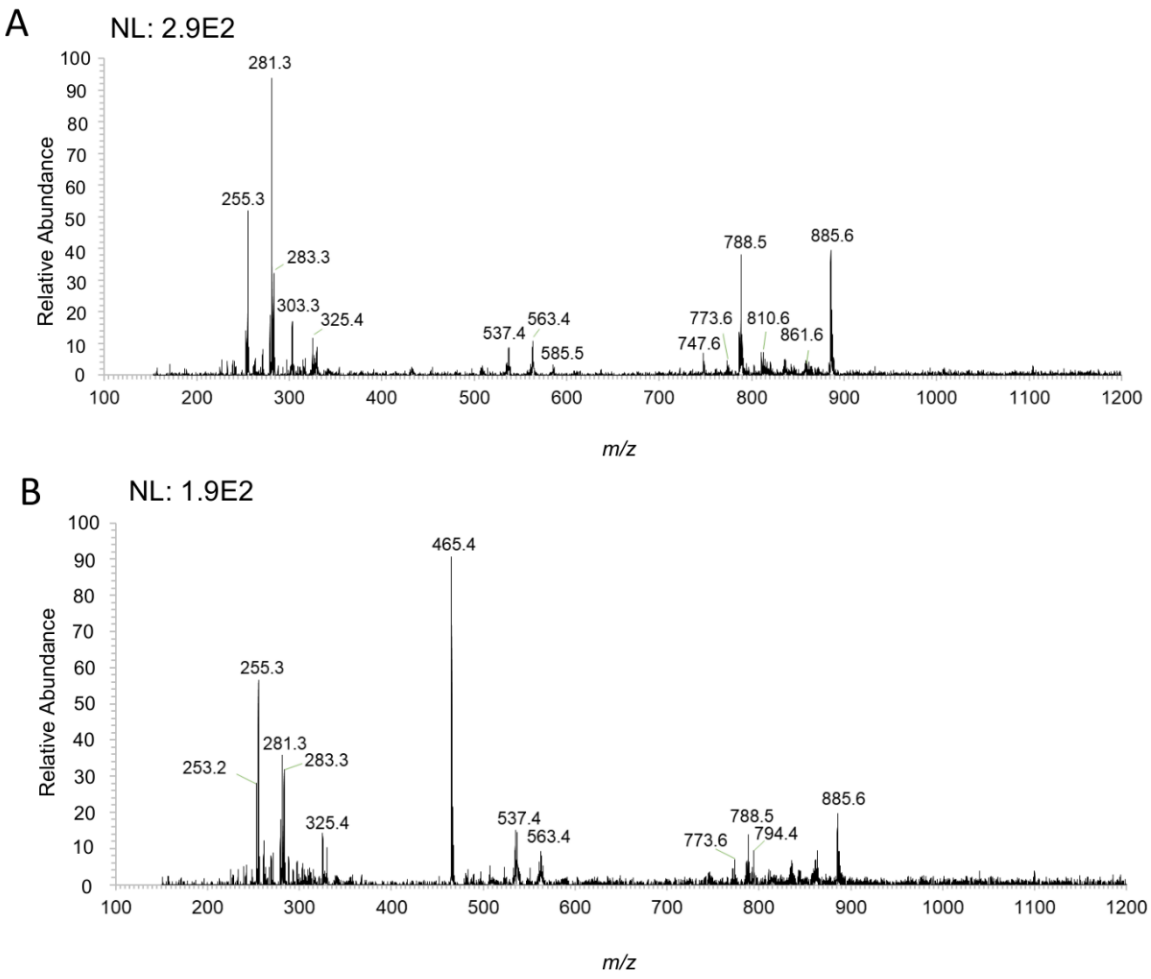

Figure S1. Representative negative mode desorption electrospray ionization mass spectrometry (DESI-MS) imaging mass spectra obtained from skin biopsy. (A) Nodular BCC aggregate from specimen #15-1372 (mass spectral average from 4 adjacent pixels). (B) Adjacent normal skin from specimen #15-1372 (mass spectral average from 16 adjacent pixels).

Table S1. High mass resolution, isotopic distribution and tandem mass spectrometry data used for identification of molecular ions.

Measured *m/z*	High mass resolution *m/z*[a]	Main Fragment Ions	Selected Isotopic peaks[b]	Tentative ion attribution[c]	Exact *m/z*	Mass error (ppm)	Proposed ion formula[d]
115.0	115.0031	71.01		Fumaric acid	115.0031	0	$C_4H_3O_4$
253.2	253.2163	235.21		FA(16:1)	253.2168	-2.0	$C_{16}H_{29}O_2$
255.3	255.2321	237.22		FA(16:0)	255.2324	-1.2	$C_{16}H_{31}O_2$
281.3	281.2475	263.24		FA(18:1)	281.2481	-2.1	$C_{18}H_{33}O_2$
283.3	283.2635	265.25		FA(18:0)	283.2637	-0.7	$C_{18}H_{35}O_2$
303.3	303.2323	259.24, 285.22		FA(20:4)	303.2324	-0.3	$C_{20}H_{31}O_2$
465.4	465.3036	--	467.2993 (^{34}S)	Cholesterol sulfate	465.3039	-0.6	$C_{27}H_{45}O_4S$
537.4	537.4875	--		Dimer [FA(18:1)+ FA(16:0)]	537.4883	-1.48	$C_{34}H_{65}O_4$
563.5	563.5026	--		Dimer [FA(18:1)+ FA(18:1)]	563.5039	-2.3	$C_{36}H_{67}O_4$
585.5	585.4867	--		Dimer [FA(18:1)+ FA(20:4)]	585.4883	-2.7	$C_{38}H_{65}O_4$
747.6	747.5156	483.27, 391.22, 281.25, 255.23		PG(16:0/18:1)	747.5176	-2.7	$C_{40}H_{76}O_{10}P$
773.6	773.5315	509.29, 417.24, 281.25		PG(18:1/18:1)	773.5333	-2.3	$C_{42}H_{78}O_{10}P$
788.5	788.5421	701.51, 419.25, 281.25, 283.27		PS(18:1/18:0)	788.5442	-2.7	$C_{42}H_{79}NO_{10}P$
792.4	792.5306	506.32, 281.25, 253.22	794.5269 (^{37}Cl)	PC(18:1/16:1)	792.5310	-0.5	$C_{42}H_{80}NO_8PCl$

794.4	794.5459	508.34, 283.26, 253.22	796.5424 (^{37}Cl)	PC(18:0/16:1)	794.5467	-1.0	$C_{42}H_{82}NO_8PCl$
810.6	810.5261	723.49, 419.25 303.23, 283.26		PS(18:0/20:4)	810.5285	-3.0	$C_{44}H_{77}NO_{10}P$
835.6	835.5316	581.31, 419.26, 283.26, 253.22		PI(16:1/18:0)	835.5337	-2.5	$C_{43}H_{80}O_{13}P$
861.6	861.5473	599.32, 581.31, 419.26, 283.26, 279.23		PI(18:2/18:0)	861.5493	-2.3	$C_{45}H_{82}O_{13}P$
885.6	885.5471	723.49, 599.32, 581.31, 439.22, 419.26, 303.23, 283.26		PI(18:0/20:4)	885.5493	-2.5	$C_{47}H_{82}O_{13}P$

[a] High mass resolution analysis was performed with the Orbitrap mass analyzer.

[b] Selected isotopic peaks listed in this column are important for molecular ion characterization. All ions have abundant isotopic peaks, such as ^{13}C peaks.

[c] FA = fatty acid, PG = glycerophosphoglycerol; PS = glycerophosphoserine; PC = glycerophosphocholine; PI = glycerophosphoinositol. (X:Y) denotes the total number of carbons and double bonds in the fatty acid chains. The most abundant isomer based on the fragments is listed.

[d] Proposed formula for the ion detected.

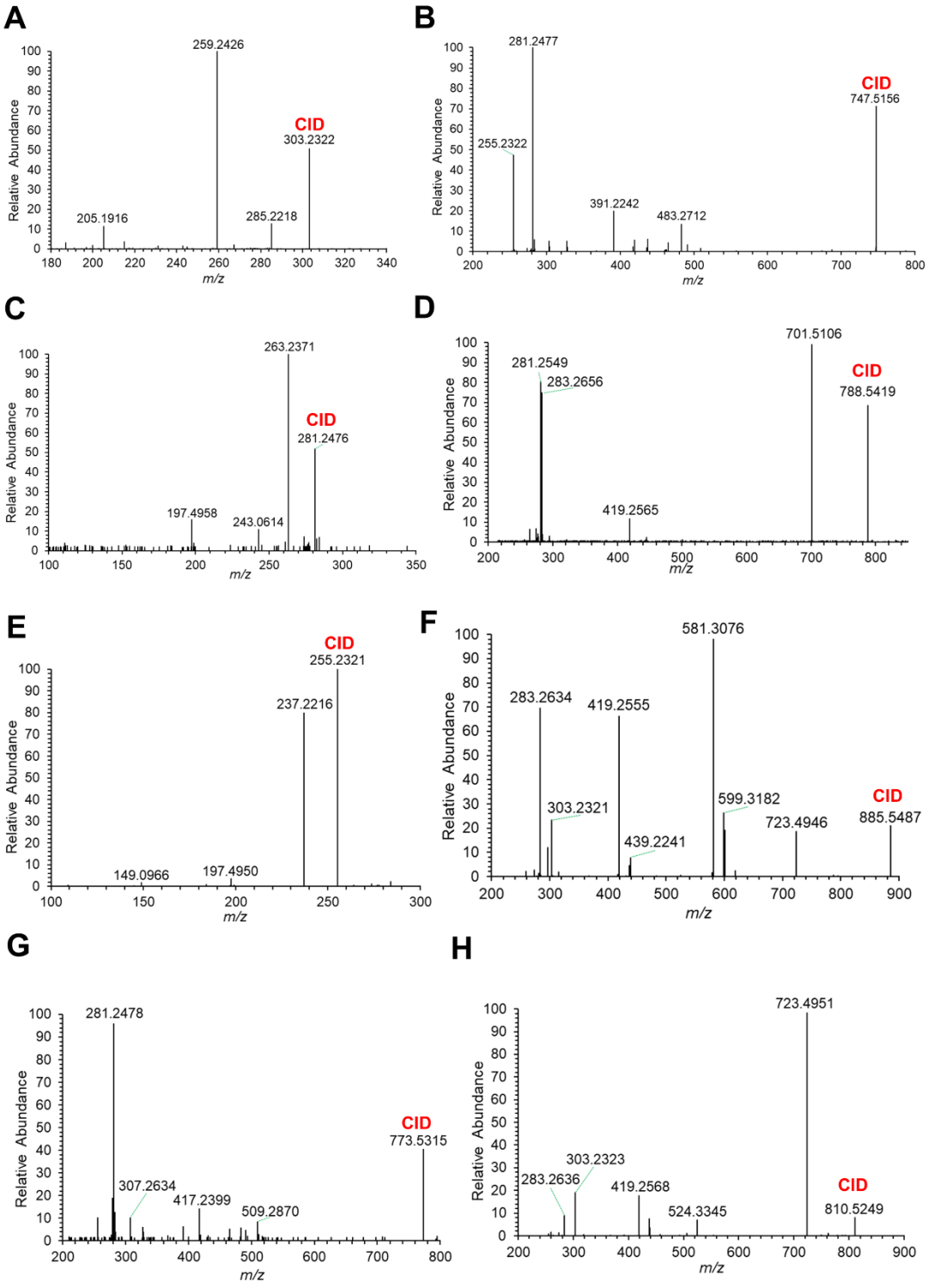

Figure S2. Tandem MS data for identified molecular ions. Collision induced dissociation, CID, was performed on the following molecular ions: (A) Arachidonic acid; (B) Glycerophosphoglycerol (16:0/18:1); (C) Oleic acid; (D) Glycerophosphoserine (18:1/18:0); (E) Palmitic acid; (F) Glycerophosphoinositol (18:0/20:4); (G) Glycerophosphoglycerol (18:1/18:1); (H) Glycerophosphoserine (18:0/20:4).

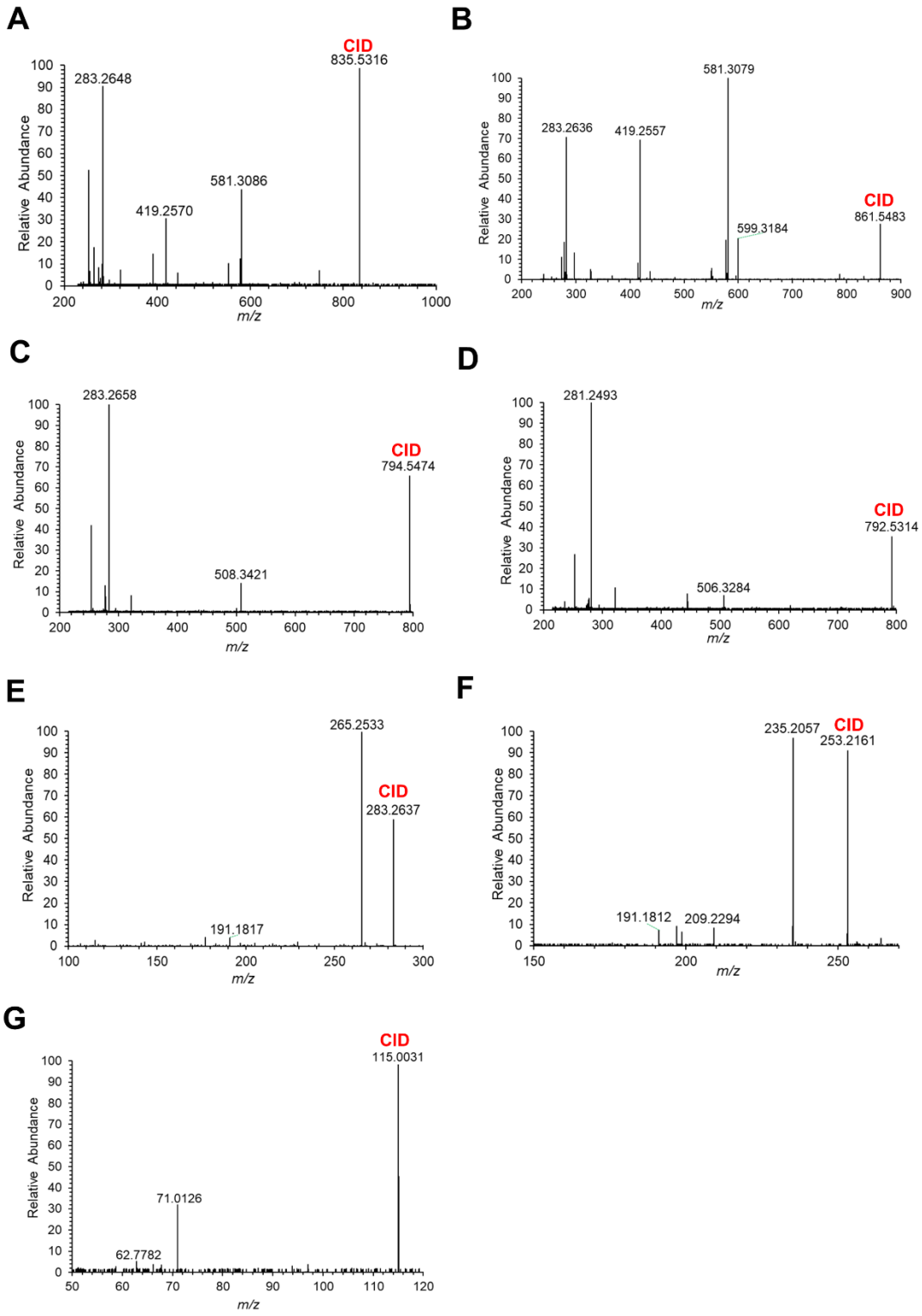

Figure S3. Tandem MS data for identified molecular ions. CID was performed on the following molecular ions: (A) Glycerophosphoinositol (16:1/18:0); (B) Glycerophosphoinositol (18:2/18:0); (C) Glycerophosphocholine (16:1/18:0); (D) Glycerophosphocholine (16:1/18:1); (E) Stearic acid; (F) Palmitoleic acid; (G) Fumaric acid.