

Analytical and Bioanalytical Chemistry

Electronic Supplementary Material

Chemical profiles of birch and alder bark by ambient mass spectrometry

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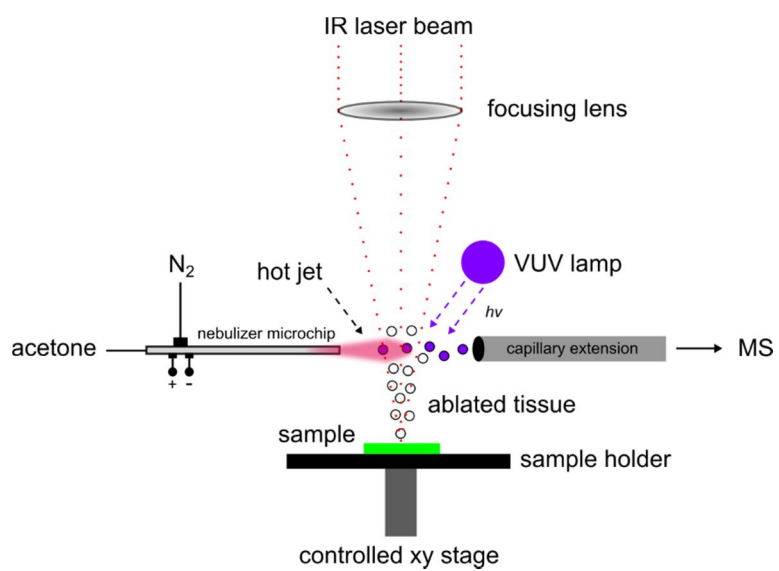


Fig. S1 A schematic picture of the LAAPPI-MSI setup

Table S1 Observed triterpenoid precursor ions and their MS² and MS³ (marked with *) fragments in direct infusion μ APPI experiments, with toluene as the dopant. The main peak of the compound was chosen as the precursor ion. Nebulizer gas (N₂) flow was 180 mL / min, microchip heated nebulizer heating power was 4.5 W, triterpenoid standard concentrations were 10 μ M in toluene infused with 5 μ L/min flow rate. Experiments were performed in positive ion mode. Only product ions with $\geq 10\%$ intensities compared to the base peak intensity in the MS² spectrum, and $\geq 20\%$ in the MS³ spectrum are presented

Triterpenoid	Precursor ion and relative intensity (%) from the base peak	Observed MS ² fragments and relative intensities (%) from the base peak
Betulin	442 M ⁺⁺ (7)	424 (100), 411 (93), 427 (68), 318 (41), 203 (29) 189 (29), 235 (23), 234 (20), 220 (20), 207 (19), 381 (17), 399 (13), 206 (13), 190 (11), 409 (11), 413 (11), 205 (10)
	424* (13)	189 (100), 381 (90), 409 (82), 204 (38), 202 (31), 136 (30), 190 (29), 406 (27), 393 (23), 187 (22), 216 (21)
Lupeol	426 M ⁺⁺ (5)	204 (100), 411 (98), 218 (89), 189 (66), 313 (36), 203 (35), 383 (34), 300 (34), 207 (22), 234 (21), 408 (20), 161 (16), 175 (16), 220 (15), 257 (14), 272 (14), 315 (13), 316 (13), 205 (13), 286 (12), 162 (12), 147 (12), 187 (11), 206 (11), 191 (11), 190 (10), 148 (10)
Betulonic acid	456 M ⁺⁺ (7)	438 (100), 234 (50), 248 (47), 189 (42), 316 (32), 220 (31), 410 (27), 207 (24), 395 (22), 302 (22), 441 (20), 202 (19), 187 (18), 203 (16), 191 (13), 219 (12), 423 (12), 190 (11)
Betulonic acid	454 M ⁺⁺ (4)	410 (100), 408 (41), 248 (34), 190 (22), 439 (17), 205 (15), 436 (14), 235 (11)
	455 [M+H] ⁺ (5)	437 (100), 409 (42), 177 (23), 411 (18), 343 (13), 391 (10), 259 (10)
Allobetulin	442 M ⁺⁺ (4)	424 (100), 411 (27), 220 (24), 371 (23), 149 (18), 399 (14), 205 (14), 189 (11)
	443 [M+H] ⁺ (5)	425 (100), 413 (31), 191 (30)
Allobetulone	441 [M+H] ⁺ (6)	423 (100), 411 (65), 329 (13), 177 (12), 245 (11)
	440 M ⁺⁺ (8)	422 (100), 410 (93), 369 (47), 220 (41), 204 (33), 148 (17), 397 (16), 199 (15), 425 (13), 205 (12), 202 (10), 391 (10), 217 (10)

Table S2 Observed betulin and allobetulin precursor ions and their MS² fragments in direct infusion μ APPI experiments, with acetone as the dopant. Nebulizer gas (N₂) flow was 180 mL / min, microchip heated nebulizer heating power was 4.5 W, triterpenoid standard concentrations were 10 μ M in acetone, infused with 5 μ L/min flow rate. Experiments were performed in positive ion mode. Only product ions with $\geq 10\%$ intensities compared to the base peak intensity in the MS² spectrum are presented

Triterpenoid	Precursor ion and relative intensity (%) from the base peak	Observed MS ² fragments and relative intensities (%) from the base peak
Betulin	425 (4)	407 (100), 219 (20), 283 (18), 217 (15), 245 (15), 201 (15), 255 (14), 269 (14), 191 (14), 257 (14), 273 (12), 227 (11), 397 (11), 215 (10)
Allobetulin	425 (6)	407 (100), 247 (63), 245 (60), 191 (50), 397 (29), 229 (26), 217 (24), 301 (21), 283 (18), 203 (17), 177 (14), 227 (14), 273 (12), 257 (12), 179 (11), 275 (11), 173 (11), 395 (10)

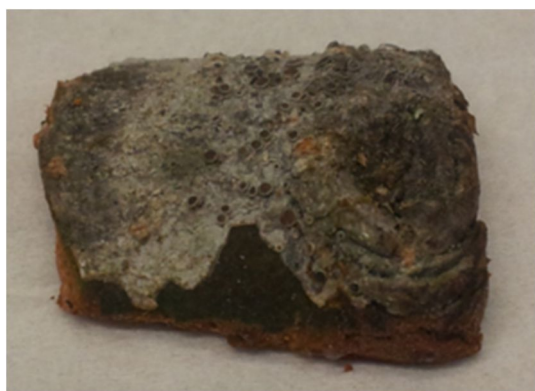


Fig. S2 *A. incana* F1 sample (mature stem)

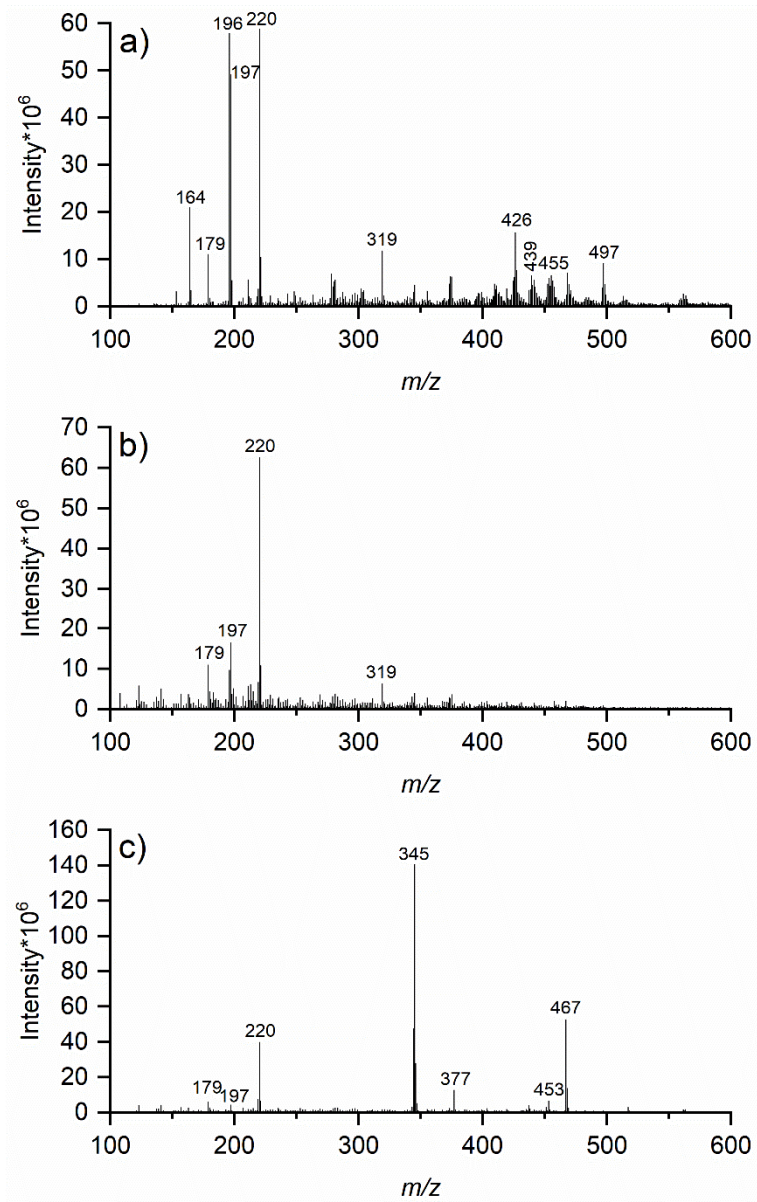


Fig. S3 *A. incana* DAPPI mass spectra from a) lenticel, b) light grey surface, and c) dark grey surface