

Supplement

Table S1. Amino acid peak assignments (TOF-SIMS). Peaks were assigned based on mass and previous studies.

Amino Acid	Mass	Chemical formula
Glycine	75	C ₂ H ₅ NO ₂
Alanine	89	C ₃ H ₇ NO ₂
Serine	105	C ₃ H ₇ NO ₃
Proline	115	C ₅ H ₉ NO ₂
Valine	117	C ₅ H ₁₁ NO ₂
Threonine	119	C ₄ H ₉ NO ₃
Leucine	131	C ₆ H ₁₃ NO ₂
Asparagine	132	C ₄ H ₈ N ₂ O ₃
Lysine	146	C ₆ H ₁₄ N ₂ O ₂
Glutamic acid	147	C ₅ H ₉ NO ₄
Methionine	149	C ₅ H ₁₁ SNO ₂
Phenylalanine	165	C ₉ H ₁₁ NO ₂
Tyrosine	181	C ₉ H ₁₁ NO ₃

Amino acid fragments		
Mass	Assignment	Source
27	C ₂ H ₃	Assigned
28	C ₂ H ₄	Assigned
29	C ₂ H ₅	Assigned
30	CH ₄ N	Orlando et al. 2013
31	CH ₃ O	Assigned
39	C ₂ HN	Colleary et al. 2021

40	C ₂ H ₂ N	Colleary et al. 2021
41	C ₃ H ₅	Colleary et al. 2021
42	C ₂ H ₄ N	Assigned
43	C ₃ H ₇	Orlando et al. 2013
44	C ₂ H ₆ N	Orlando et al. 2013
55	C ₃ H ₅ N	Colleary et al. 2021
56	C ₃ H ₆ N	Orlando et al. 2013
57	C ₄ H ₉	Colleary et al. 2021
59	CN ₃ H ₅ or C ₃ H ₇ O	Orlando et al. 2013
60	C ₂ H ₆ NO or C ₃ H ₈ O	Orlando et al. 2013
61	C ₂ H ₅ S	Orlando et al. 2013
63	CH ₅ NO ₂	Assigned
67	C ₄ H ₅ N	Colleary et al. 2021
68	C ₄ H ₆ N	Orlando et al. 2013
69	C ₄ H ₅ O or C ₂ H ₃ N ₃	Orlando et al. 2013
70	C ₅ H ₁₀	Assigned
71	C ₃ H ₃ O ₂	Orlando et al. 2013
72	C ₄ H ₁₀ N	Orlando et al. 2013
74	C ₃ H ₈ NO	Orlando et al. 2013
76	C ₂ H ₆ NS or C ₅ H ₂ N	Orlando et al. 2013
81	C ₄ H ₅ N ₂ or C ₅ H ₇ N	Orlando et al. 2013
82	C ₄ H ₆ N ₂ or C ₃ N ₄ N ₄ O	Orlando et al. 2013
83	C ₅ H ₉ N	Orlando et al. 2013
84	C ₅ H ₁₀ N	Assigned
85	C ₅ H ₁₁ N	Colleary et al. 2021
86	C ₅ H ₁₂ N	Assigned
87	C ₃ H ₇ N ₂ O or C ₃ H ₉ N ₃	Orlando et al. 2013

88	$\text{C}_3\text{H}_6\text{NO}_2$ or $\text{C}_6\text{H}_2\text{N}$	Orlando et al. 2013
91	C_7H_7	Orlando et al. 2013
92	$\text{C}_2\text{H}_8\text{N}_2\text{O}_2$	Assigned
93	$\text{C}_3\text{H}_{11}\text{NO}_2$	Colleary et al. 2021
95	$\text{C}_5\text{H}_5\text{NO}$	Colleary et al. 2021
96	CaCO_2	Colleary et al. 2021
97	$\text{C}_4\text{H}_3\text{NO}_2$	Colleary et al. 2021
98	$\text{C}_4\text{H}_4\text{NO}_2$	Orlando et al. 2013
100	$\text{C}_4\text{H}_{10}\text{N}_3$	Orlando et al. 2013
102	$\text{C}_4\text{H}_8\text{NO}_2$	Orlando et al. 2013
103	$\text{C}_4\text{H}_9\text{NO}_2$	Colleary et al. 2021
104	$\text{C}_4\text{H}_{10}\text{NS}$ or C_8H_8	Orlando et al. 2013
107	$\text{C}_7\text{H}_7\text{O}$	Orlando et al. 2013
108	$\text{C}_3\text{H}_{12}\text{N}_2\text{O}_2$	Assigned
109	$\text{C}_7\text{H}_{11}\text{N}$	Colleary et al. 2021
110	$\text{C}_5\text{H}_8\text{N}_3$	Orlando et al. 2013
111	$\text{C}_5\text{H}_9\text{N}_3$	Colleary et al. 2021
112	$\text{C}_5\text{H}_{10}\text{N}_3$	Colleary et al. 2021
113	$\text{C}_6\text{H}_{11}\text{NO}$	Colleary et al. 2021
116	$\text{C}_4\text{H}_8\text{N}_2\text{O}_2$	Assigned
118	$\text{C}_4\text{H}_{10}\text{N}_2\text{O}_2$	Assigned
120	$\text{C}_8\text{H}_{10}\text{N}$	Orlando et al. 2013
121	$\text{C}_8\text{H}_{11}\text{N}$	Assigned
122	$\text{C}_7\text{H}_8\text{NO}$	Colleary et al. 2021
124	$\text{C}_3\text{H}_{14}\text{N}_3\text{O}_2$	Assigned
127	$\text{C}_5\text{H}_{11}\text{N}_4$	Orlando et al. 2013
128	$\text{C}_6\text{H}_{10}\text{NO}_2$	Assigned

129	C ₁₀ H ₉	Assigned
130	C ₉ H ₈ N	Orlando et al. 2013
138	C ₆ H ₆ NO ₂	Colleary et al. 2021
141	C ₆ H ₉ N ₂ O ₂	Colleary et al. 2021
150	C ₉ H ₁₀ O ₂	Assigned
152	C ₆ H ₈ NO ₂	Colleary et al. 2021
159	C ₁₀ H ₁₁ N ₂	Orlando et al. 2013
168	C ₈ H ₁₀ NO ₃	Colleary et al. 2021
169	C ₈ H ₁₁ NO ₃	Colleary et al. 2021
171	C ₆ H ₁₁ N ₄ O ₂	Colleary et al. 2021
174	Ca ₂ PO ₄	Assigned
175	C ₉ H ₅ NO ₃	Colleary et al. 2021
177	C ₉ H ₇ NO ₃	Colleary et al. 2021

Table S2. H:C and O:C ranges for biochemical classification (FTICR-MS)

Compound class	O/C	H/C range
Amino sugar and carbohydrate	0.5~0.7	0.8~2.5
Condensed aromatic	0.0~0.4	0.2~0.8
Lignin	0.29~0.65	0.7~1.5
Lipid	0.0~0.3	1.5~2.5
Protein	0.3~0.6	1.5~2.3
Tannin	0.65~1.00	0.8~1.5
Unsaturated hydrocarbon	0.0~0.3	1.0~1.6