SUPPORTING INFORMATION

Lignin as a MALDI matrix for small molecules：A proof of concept

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[1] Equal contribution to this work.

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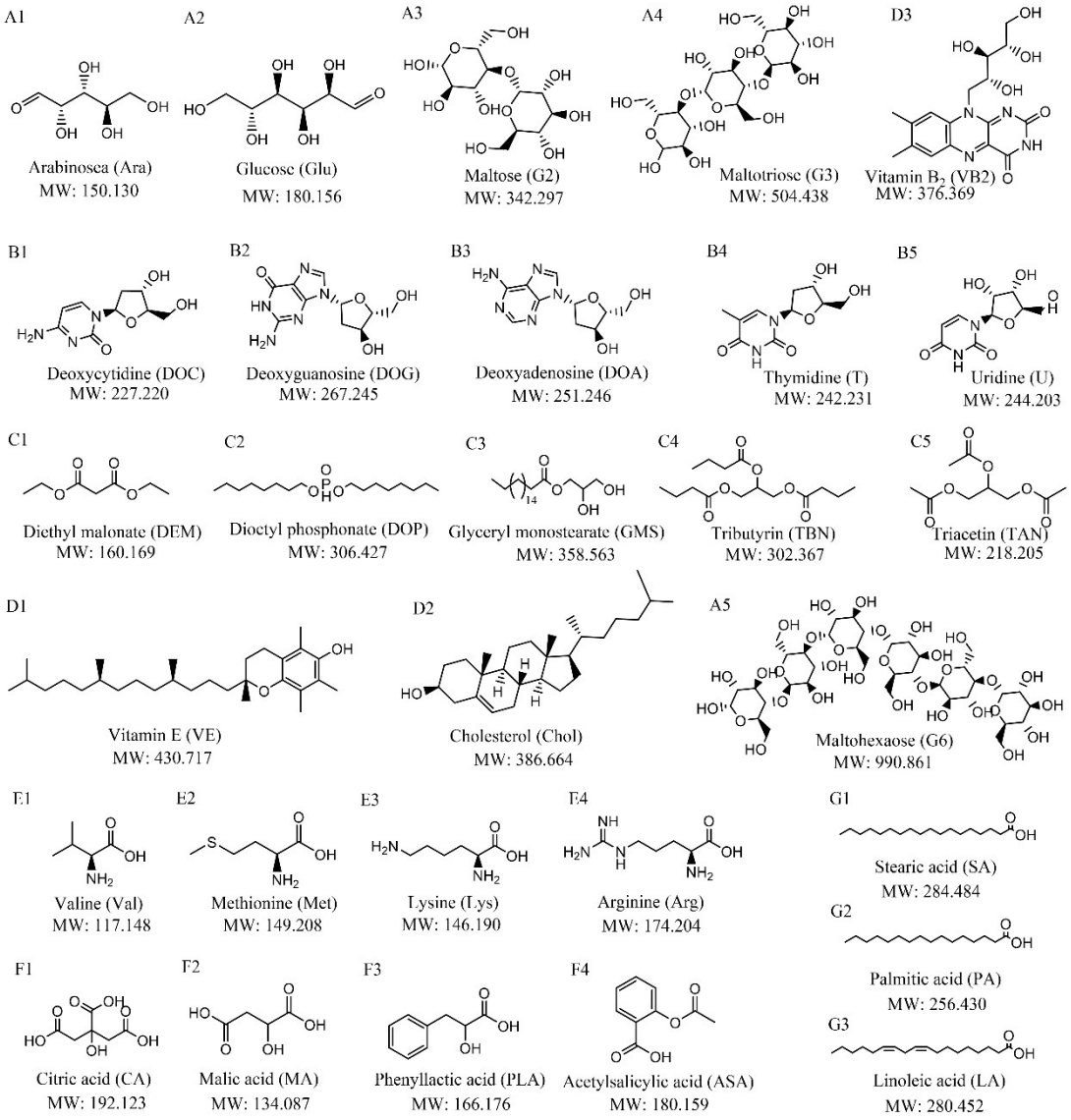
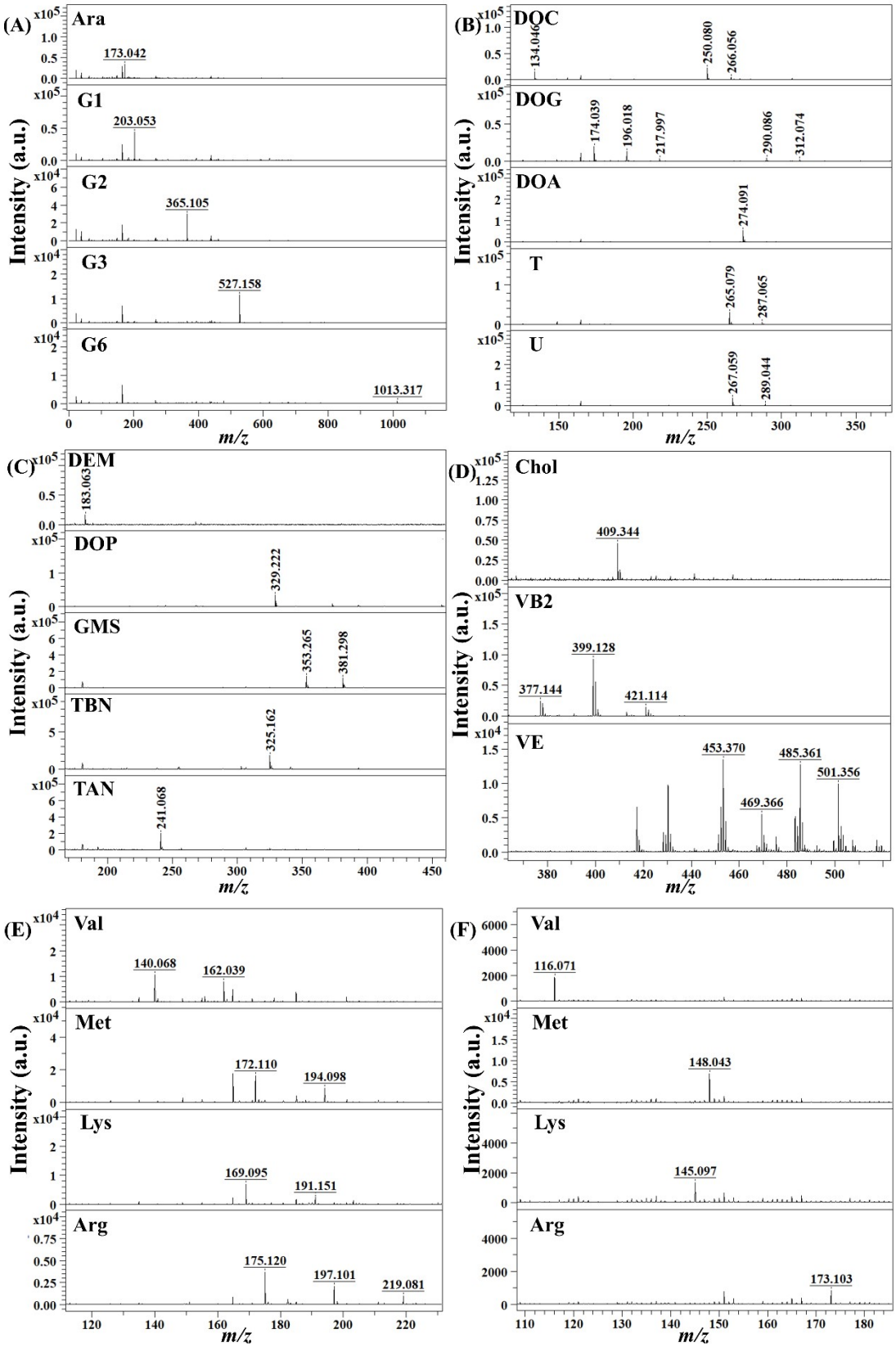


Figure S1. Chemical structures of detected small molecules classified by different capitals.


(A)
Ara
173.042
G1
203.053
G2
365.105
G3
527.158
G6
1013.317
Intensity (a.u.)
m/z
(B)
DOC
134.046
250.080
266.056
DOG
174.039
196.018
217.997
290.086
312.074
DOA
274.091
T
265.079
287.065
U
267.059
289.044
(C)
DEM
183.063
DOP
329.222
GMS
353.265
381.298
TBN
325.162
TAN
241.068
(D)
Chol
409.344
VB2
399.128
377.144
421.114
VE
453.370
485.361
501.356
469.366
(E)
Val
140.068
162.039
Met
172.110
194.098
Lys
169.095
191.151
Arg
175.120
197.101
219.081
(F)
Val
116.071
Met
148.043
Lys
145.097
Arg
173.103

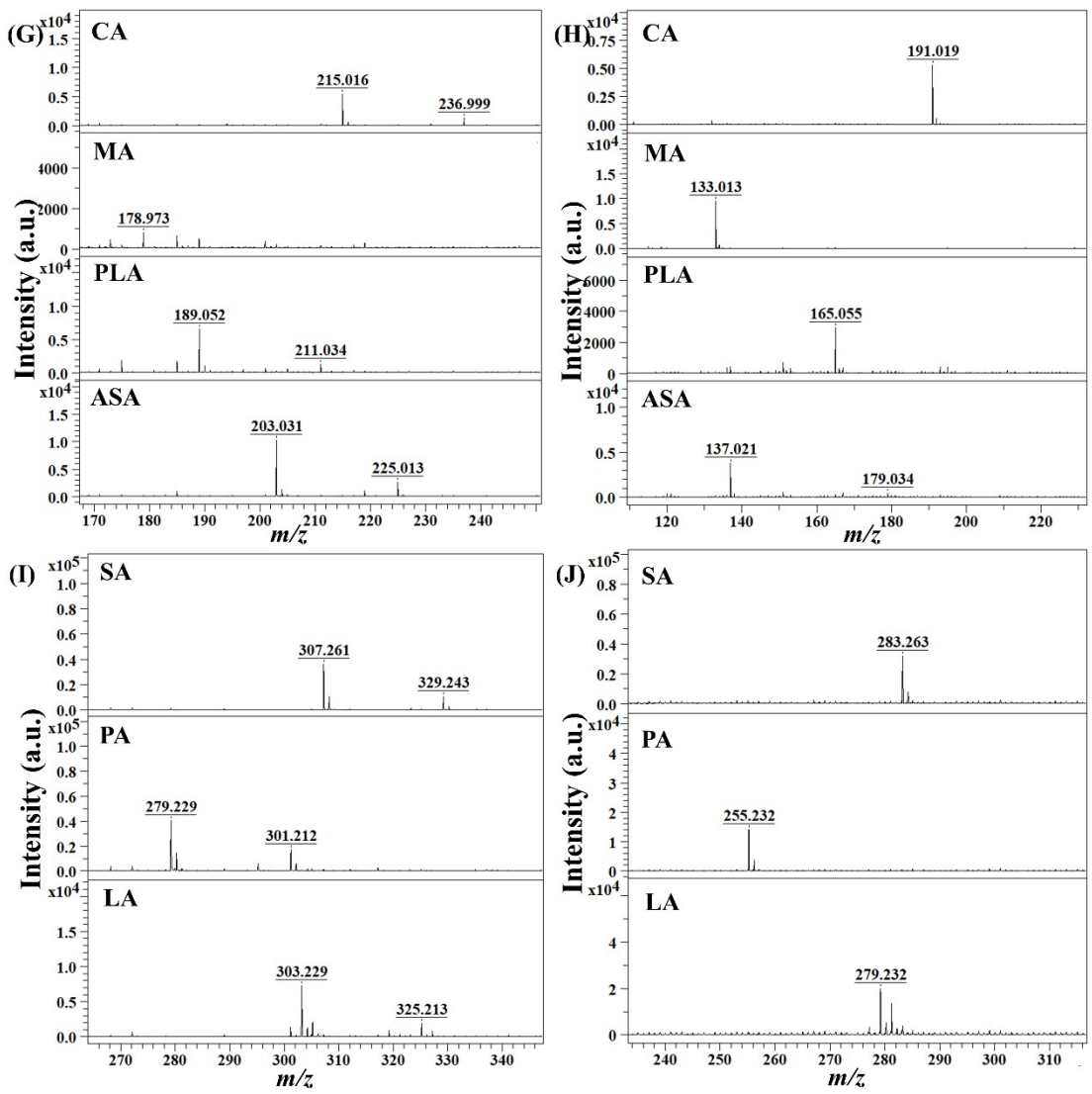


Figure S2. MALDI spectrum for qualitative results of oligosaccharides (A), glycosides(B), esters (C), vitamins (D), amino acids (E, F), hydroxy acids (G, H), and fatty acids (I, J) by DAL matrix in positive (A-D, E, G, I) and negative (F, H, J) modes.

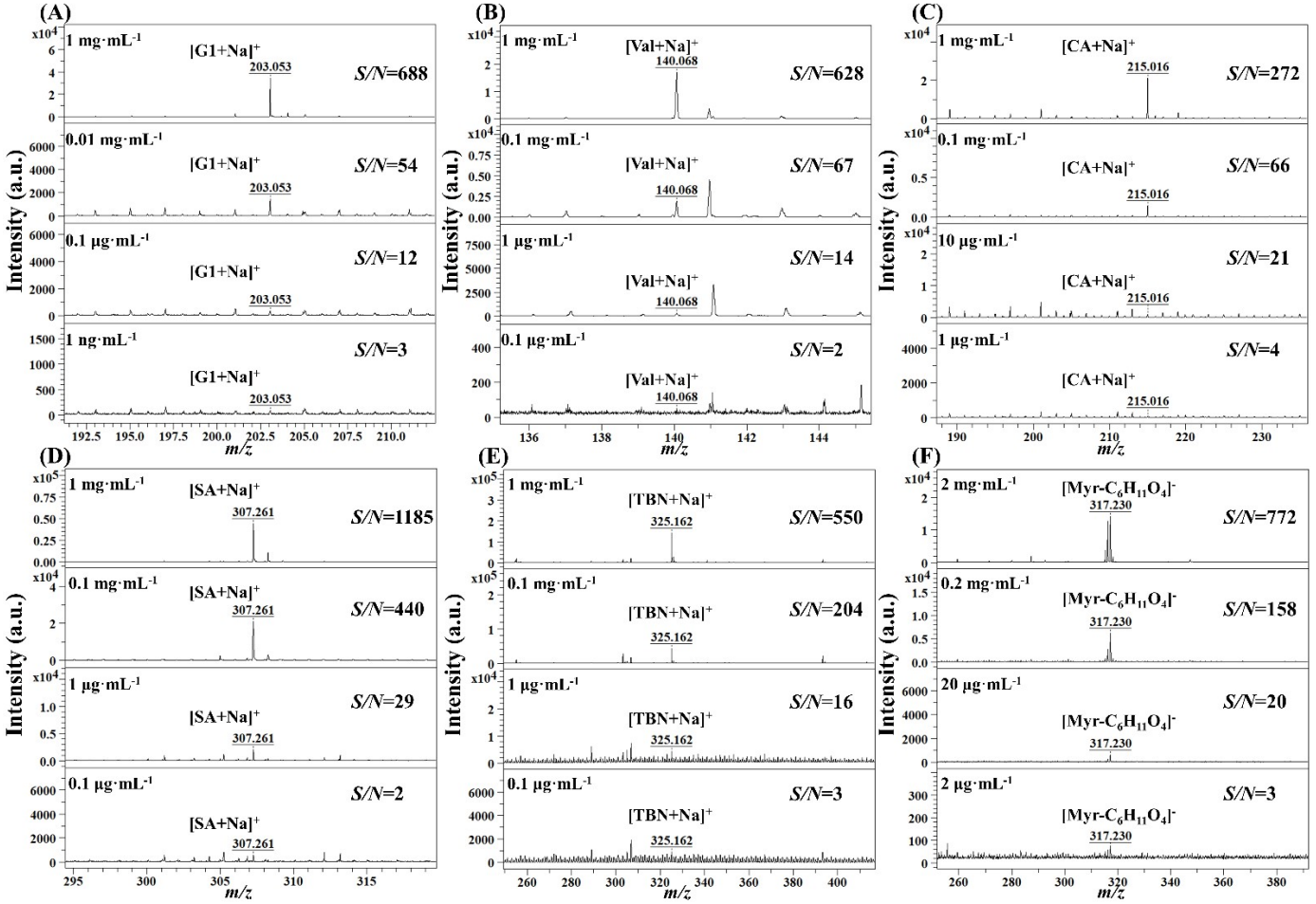


Figure S3. MALDI-TOF spectrums for different molecules with different concentrations, G1 (A), Val (B), CA (C), SA (D), and TBN (E) in positive mode, and Myr (F) in negative mode.

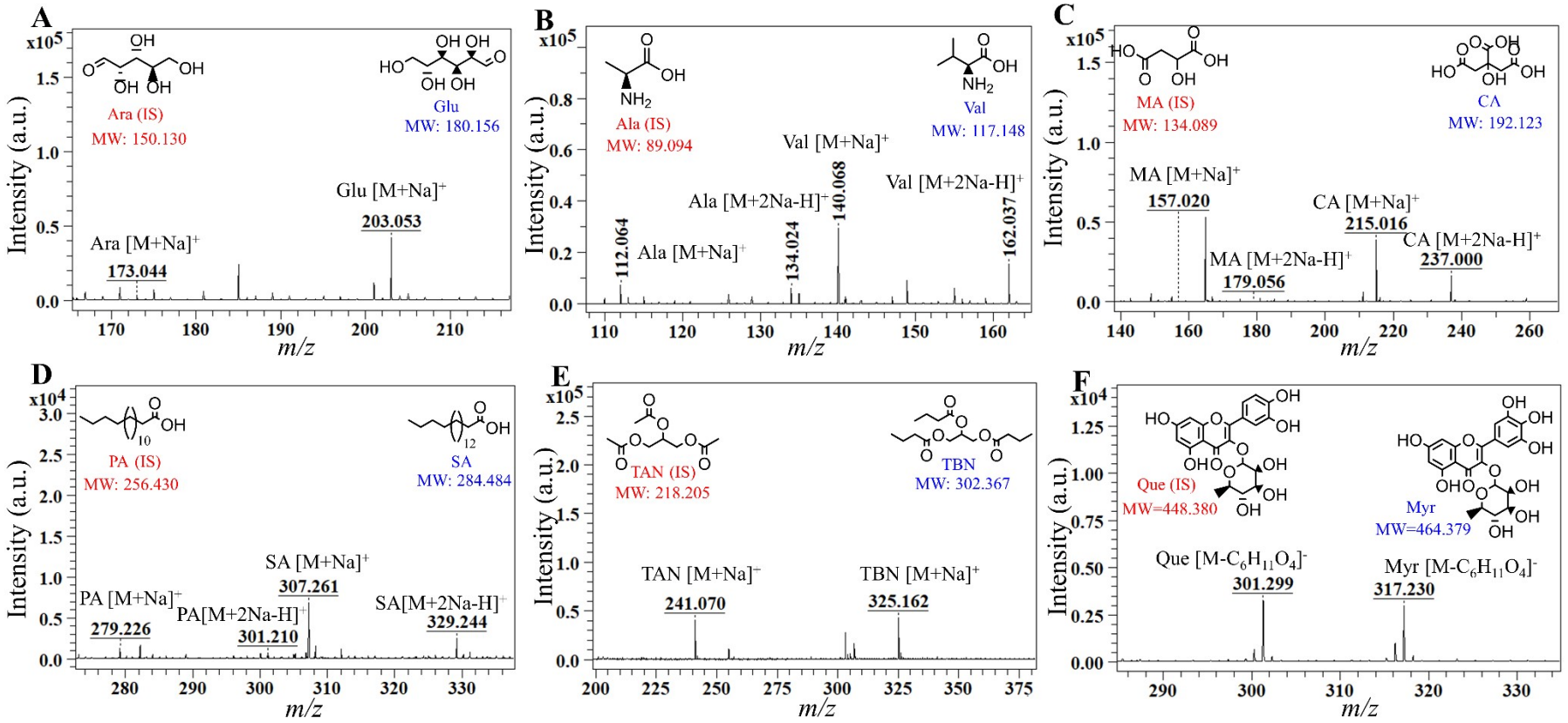


Figure S4. MALDI-TOF spectrums for different molecules spiked with their own IS, G1 (A), Val (B), CA (C), SA (D), and TBN (E) in positive mode, and Myr (F) in negative mode.

Table.S1 Peak assignment of small molecules by MALDI using DAL as matrix.

Mode		Chemicals	Peak Assignment
Positive	oligosaccharides	Ara	173.042$[M+Na]^+$
		G1	203.053$[M+Na]^+$
		G2	365.105$[M+Na]^+$
		G3	527.158$[M+Na]^+$
		G6	1013.317$[M+Na]^+$
	glycosides	DOC	134.046$[Cytosine+Na]^+$, 250.080$[M+Na]^+$, 266.056$[M+2Na-H]^+$
		DOG	174.039$[Guanine+Na]^+$, 196.018$[Guanine+2Na-H]^+$, 217.997$[Guanine+3Na-2H]^+$, 290.086$[M+Na]^+$, 312.074$[M+2Na-H]^+$
		DOA	274.091$[M+Na]^+$
		T	265.079$[M+Na]^+$, 287.065$[M+2Na-H]^+$
		U	267.059$[M+Na]^+$, 289.044$[M+2Na-H]^+$
	esters	DEM	183.063$[M+Na]^+$
		DOP	329.222$[M+Na]^+$
		GMS	381.298$[M+Na]^+$
		TBN	325.162$[M+Na]^+$
		TAN	241.068$[M+Na]^+$
	vitamins	VE	453.370$[M+Na]^+$, 469.366$[M+K]^+$, 485.361$[M+2Na-H]^+$, 501.356$[M+Na+K-H]^+$
		Chol	409.344$[M+Na]^+$
		VB2	377.144$[M+H]^+$, 399.128$[M+Na]^+$, 421.114$[M+2Na-H]^+$
	amino acids	Val	140.068$[M+Na]^+$, 162.039$[M+2Na-H]^+$
		Met	172.040[M+Na]+, 194.020$[M+2Na-H]^+$
		Lys	169.095[M+Na]+, 191.151$[M+2Na-H]^+$
		Arg	175.120$[M+H]^+$, 197.101$[M+Na]^+$, 219.081$[M+2Na-H]^+$
	amino acids	CA	215.016$[M+Na]^+$, 236.999$[M+2Na-H]^+$
		MA	157.011$[M+Na]^+$, 178.973$[M+2Na-H]^+$
		PLA	189.052$[M+Na]^+$, 211.034$[M+2Na-H]^+$
		ASA	203.031$[M+Na]^+$, 225.013$[M+2Na-H]^+$
	fatty acids	SA	307.261$[M+Na]^+$, 329.243$[M+2Na-H]^+$
		PA	279.229$[M+Na]^+$, 301.212$[M+2Na-H]^+$
		LA	303.229$[M+Na]^+$, 325.213$[M+2Na-H]^+$
Negative	amino acids	Val	116.071$[M-H]^-$
		Met	148.043$[M-H]^-$
		Lys	145.097$[M-H]^-$
		Arg	173.103$M-H]^-$
	amino acids	CA	191.09$[M-H]^-$
		MA	133.013$[M-H]^-$
		PLA	165.055$[M-H]^-$
		ASA	137.021$[M-C2H3O]^-$, 179.034$[M-H]^-$
	fatty acids	SA	283.263$[M-H]^-$
		PA	255.232$[M-H]^-$
		LA	279.232$[M-H]^-$

Table S2. Quantification results of Myr by HPLC and MALDI.

Note: The standard regression equations of HPLC and MALDI are y = 14680x + 117002 and y = 4.8648x - 0.0359, respectively.

Name	Concentration by HPLC / ($mg \cdot mL^{-1}$)	Concentration by MALD / ($mg \cdot mL^{-1}$)	Absolute content by HPLC / ($mg \cdot g^{-1}$)	Absolute content by MALDI / ($mg \cdot g^{-1}$)
WM-L1	0.4334	0.4355	8.6689	8.7101
WM-L2	0.3820	0.3821	7.6406	7.6426
WM-L3	0.3876	0.3889	7.7512	7.7775
WM-L4	0.3827	0.3679	7.6543	7.3570
TZM-L1	0.6136	0.6185	12.2713	12.3698
TZM-L2	0.6335	0.6286	12.6704	12.5710
TZM-L3	0.6592	0.6634	13.1843	13.2680
TZM-L4	0.6428	0.6463	12.8552	12.9257
RSAHB-L1	0.5858	0.5913	11.7160	11.8268
RSAHB-L2	0.6353	0.6276	12.7060	12.5516
RSAHB-L3	0.6467	0.6482	12.9349	12.9638
RSAHB-L4	0.5200	0.5126	10.4006	10.2520
WM-S1	0.3862	0.3856	7.7236	7.7129
WM-S2	0.3850	0.3851	7.6998	7.7021
WM-S3	0.4164	0.4133	8.3278	8.2660
WM-S4	0.4169	0.4203	8.3376	8.4061
TZM-S1	0.2881	0.2875	5.7622	5.7505
TZM-S2	0.2867	0.2834	5.7347	5.6680
TZM-S3	0.3023	0.3018	6.0464	6.0360
TZM-S4	0.3118	0.3166	6.2357	6.3330
RSAHB-S1	0.4525	0.4362	9.0497	8.7231
RSAHB-S2	0.4584	0.4593	9.1684	9.1854
RSAHB-S3	0.5197	0.5217	10.3939	10.4347
RSAHB-S4	0.5304	0.5322	10.6084	10.6444

Abbreviations

AL: Alkali lignin; Ala: L-alanine; Ara: L-arabinose; Arg: L-arginine; ASA: Acetylsalicylic acid; CA: Citric acid; Chol: Cholesterol; DAL: Dealkaline lignin;

DEM: Diethyl malonate; DOA: 2'-deoxyadenosine; DOC: 2'-deoxycytidine; DOG: 2'-deoxyguanosine; DOP: Dioctyl phosphonate; EV: Ethyl vanillin; G1: D-glucose; G2: Maltose; G3: Maltotriose; G6: Maltohexose; GMS: Glyceryl monostearate; LA: Linoleic acid; Lys: L-lysine; MA: DL-malic acid; Met: L-methionine; Myr: Myricitrin; PA: Palmitic acid; PLA: D-phenyllactic acid; Que: Quercitrin; RSAHB: 'Ruan Si An Hai Bian'; SA: Stearic acid; T: Thymidine; TAN: Triacetin; TBN: Tributyrin; TZM: 'Te Zao Mei'; U: Uridine; Val: L-valine; VB2: Riboflavin; VE: Vitamin-E; WM: 'Wu Mei'.