Supplemental Data

Figure S1. SEM images of HBAX in hull-less barley: a) 3000 × and b) 5000 ×.

Figure S2. FT-IR spectrum of HBAX in hull-less barley.

Figure S3. The total ion chromatography of PMAAs derivatives (a) and mass spectra (b–m) of HBAX-60. b: 1,4-di-*O*-acetyl-2,3,5-tri-*O*-methyl arabinitol; c: 1,5-di-*O*-acetyl-2,3,4-tri-*O*-methyl xylitol; d: 1,2,4-tri-*O*-acetyl-3,5-di-*O*-methyl arabinitol; e: 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methyl glucitol; f: 1,3,4-tri-*O*-acetyl-2,5-di-*O*-methyl arabinitol; g: 1,4,5-tri-*O*-acetyl-2,3-di-*O*-methyl arabinitol; h: 1,4,5-tri-*O*-acetyl-2,3-di-*O*-methyl xylitol; i: 1,3,5-tri-*O*-acetyl-2,4,6-tri-*O*-methyl glucitol; j: 1,4,5-tri-*O*-acetyl-2,3,6-tri-*O*-methyl glucitol; k: 1,2,4,5-tera-*O*-acetyl-3-*O*-methyl xylitol; l: 1,3,4,5-tri-*O*-acetyl-2-*O*-methyl xylitol; and m: 1,2,3,4,5-penta-*O*-acetyl-xylitol. The PMAAs were derived from individual sugars, e.g., 1,5-di-*O*-acetyl-2,3,4-tri-*O*-methyl xylitol means that xylose was methylated at the *O*-2,3,4 sites and acetyled at the *O*-1,5 sites, which indicates that the corresponding linkage pattern was Xyl*p*-(1→.

Figure S4. TOCSY (a) and NOESY (b) spectra of HBAX-60.

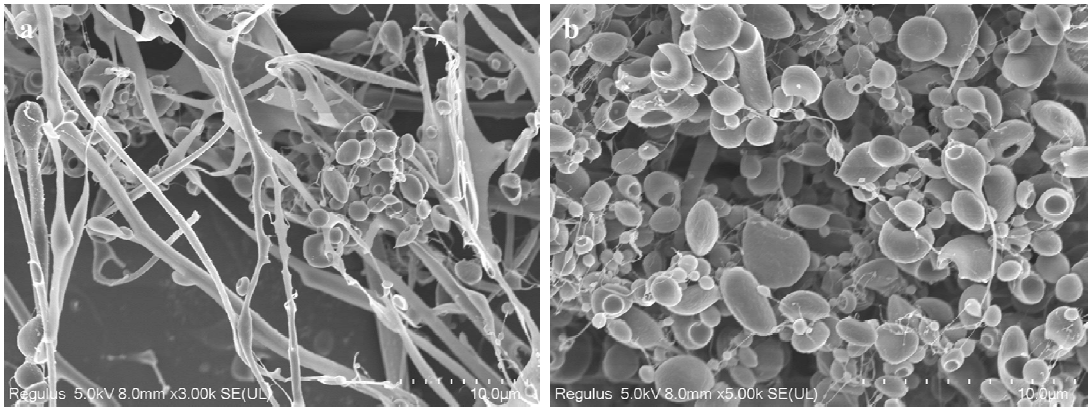


Figure S1. SEM images of HBAX in hull-less barley: (**a**) 3000 × and (**b**) 5000 ×.

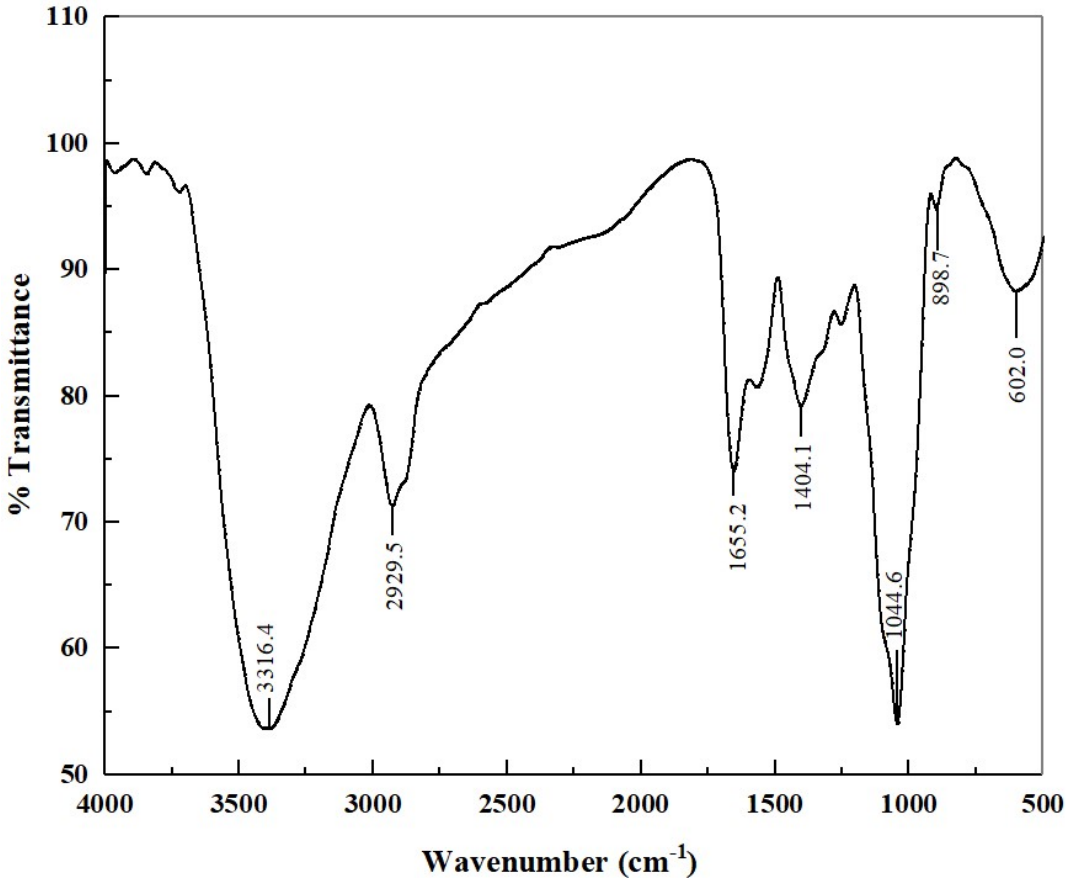
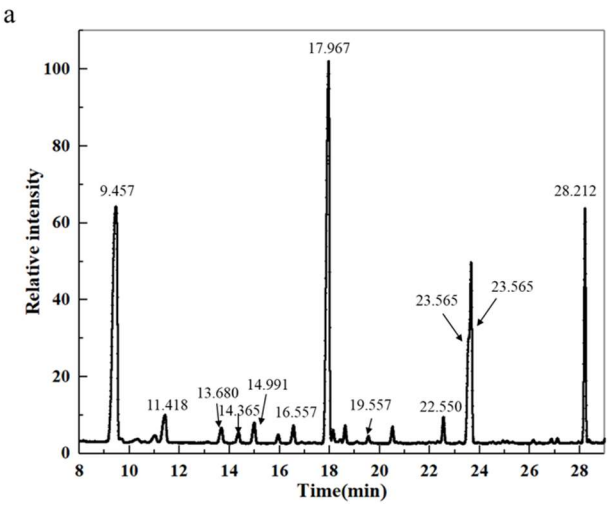
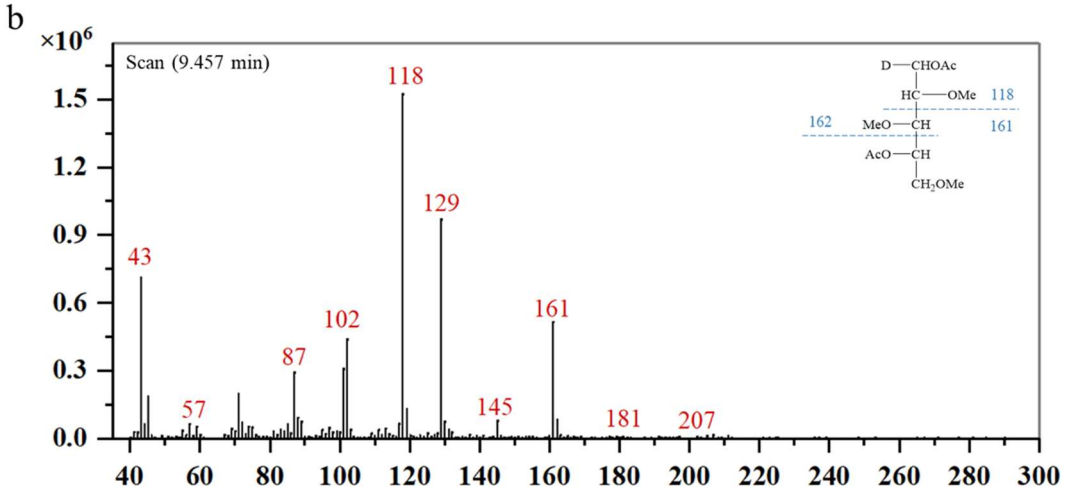
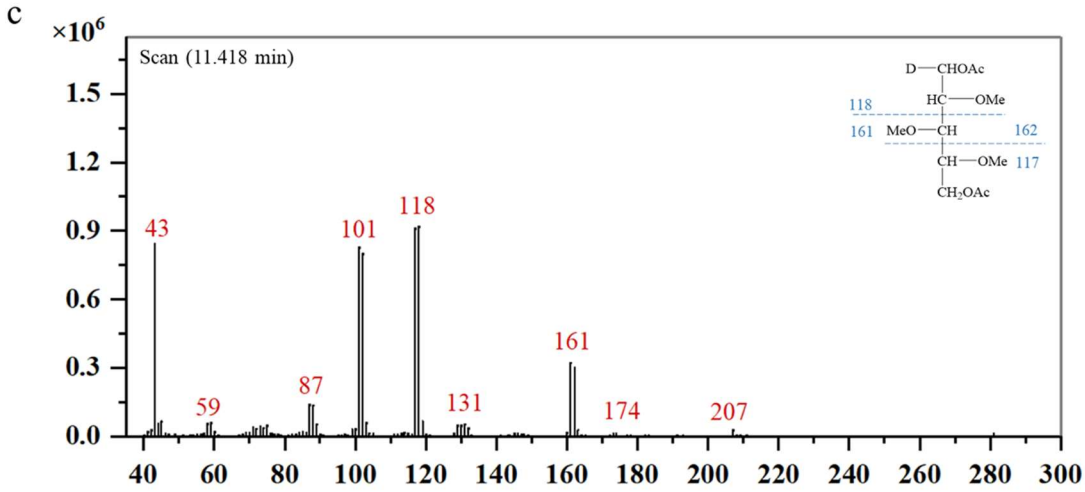


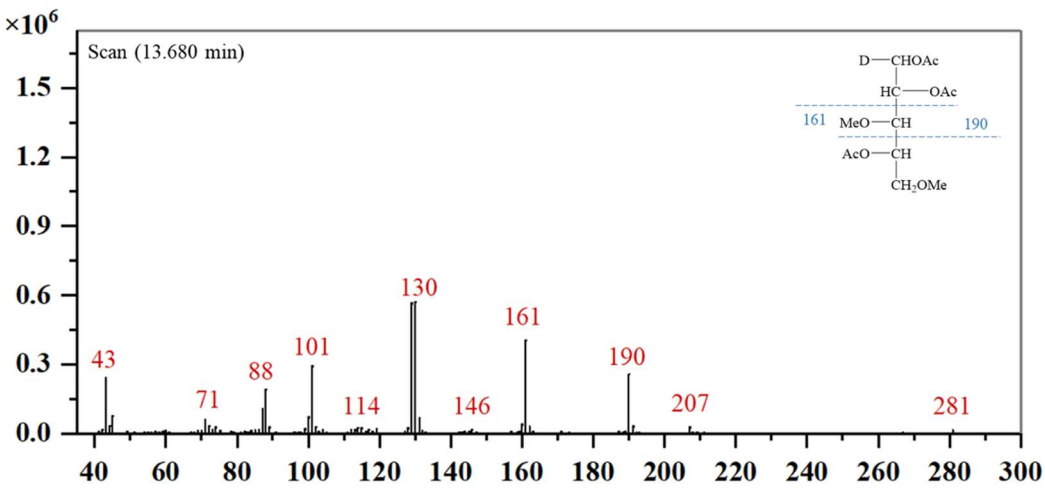
Figure S2. FT-IR spectrum of HBAX in hull-less barley.


a
Relative intensity
Time(min)
9.457
11.418
13.680
14.365
14.991
16.557
17.967
19.557
22.550
23.565
23.565
28.212

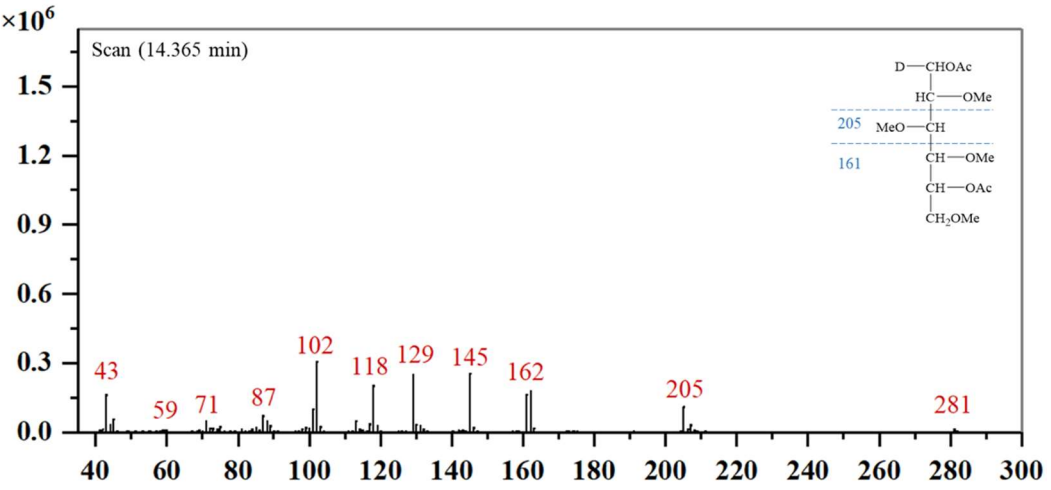

b
×10⁶
Scan (9.457 min)
118
129
43
102
87
161
57
145
181
207
D—CHOAc
HC—OMe
MeO—CH
AcO—CH
CH₂OMe
118
162
161


c
×10⁶
Scan (11.418 min)
43
101
118
161
87
59
131
174
207
D—CHOAc
HC—OMe
MeO—CH
CH—OMe
CH₂OAc
118
161
162
117

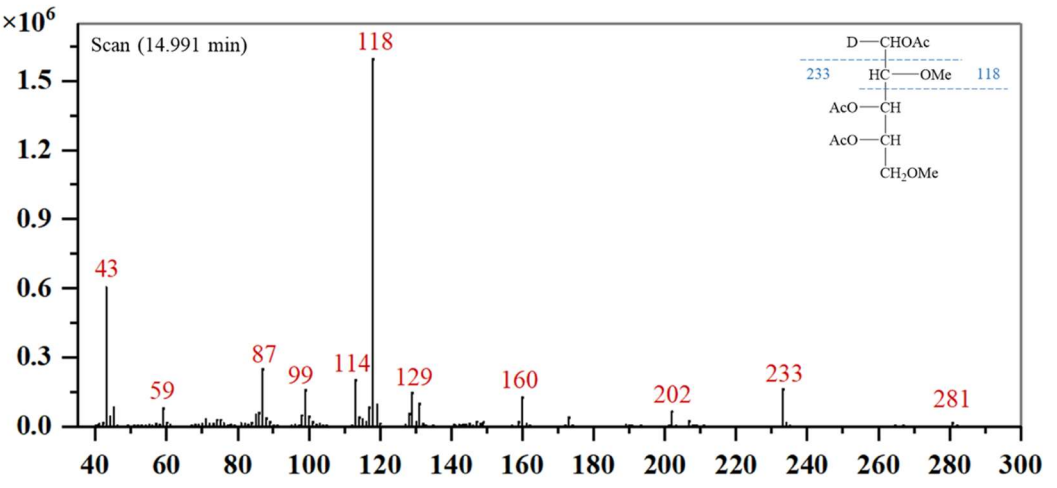
d


×10^6
Scan (13.680 min)
1.5
1.2
0.9
0.6
0.3
0.0
43
71
88
101
114
130
146
161
190
207
281
40 60 80 100 120 140 160 180 200 220 240 260 280 300
D—CHOAc
HC—OAc
161
MeO—CH
190
AcO—CH
CH2OMe

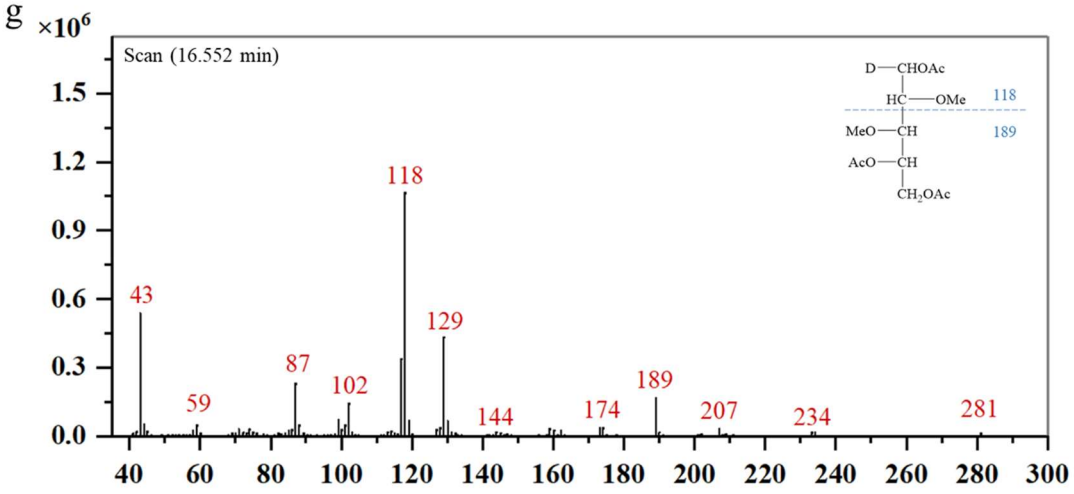
e


×10^6
Scan (14.365 min)
1.5
1.2
0.9
0.6
0.3
0.0
43
59
71
87
102
118
129
145
162
205
281
40 60 80 100 120 140 160 180 200 220 240 260 280 300
D—CHOAc
HC—OMe
205
MeO—CH
CH—OMe
161
CH—OAc
CH2OMe

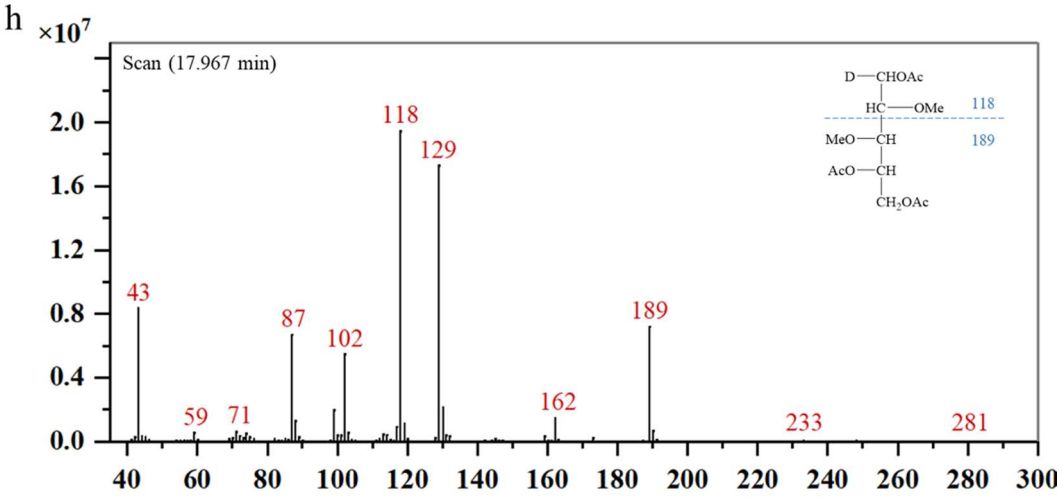
f


×10^6
Scan (14.991 min)
1.5
1.2
0.9
0.6
0.3
0.0
43
59
87
99
114
118
129
160
202
233
281
40 60 80 100 120 140 160 180 200 220 240 260 280 300
D—CHOAc
233
HC—OMe
118
AcO—CH
AcO—CH
CH2OMe

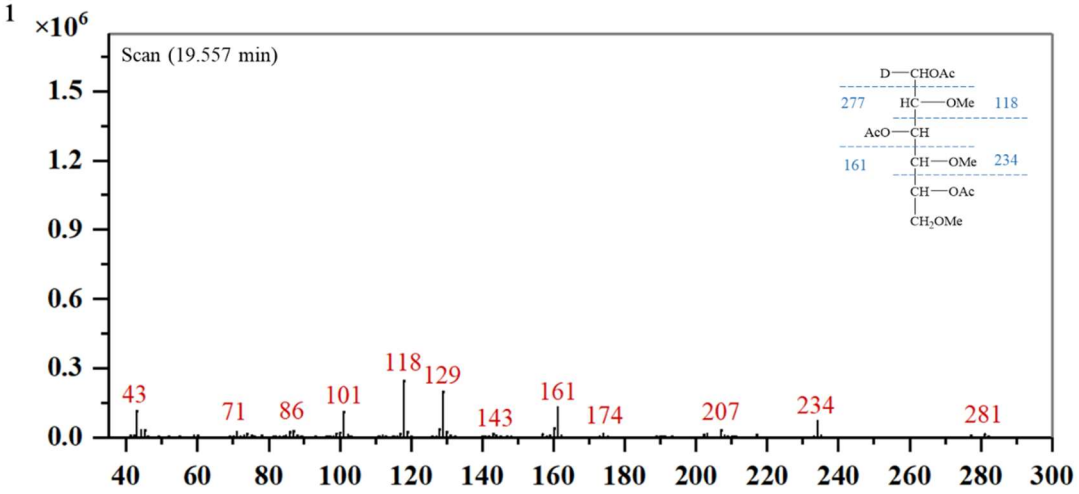
g


×10^6
Scan (16.552 min)
1.5
1.2
0.9
0.6
0.3
0.0
43
59
87
102
118
129
144
174
189
207
234
281
40 60 80 100 120 140 160 180 200 220 240 260 280 300
D—CHOAc
HC—OMe
118
MeO—CH
189
AcO—CH
CH2OAc

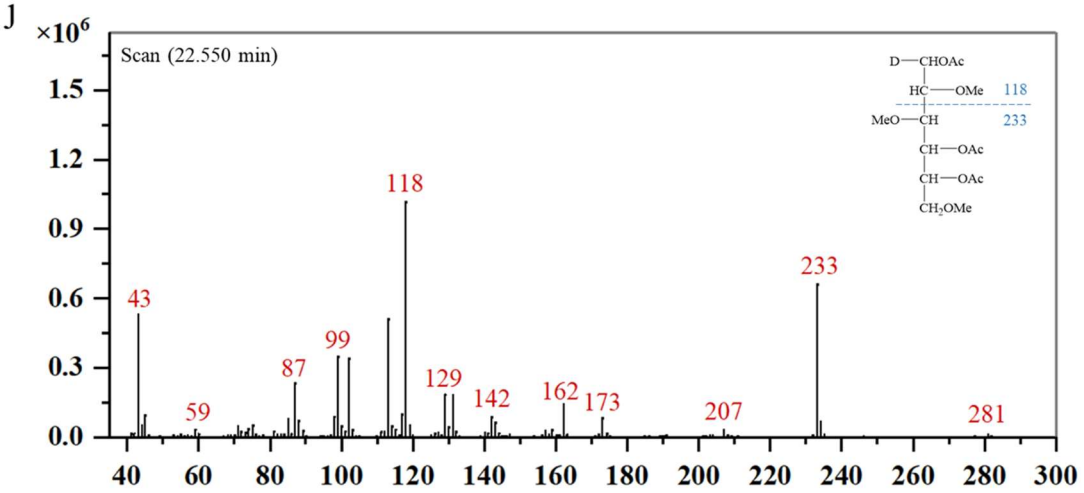
h


×10^7
Scan (17.967 min)
2.0
1.6
1.2
0.8
0.4
0.0
43
59
71
87
102
118
129
162
189
233
281
40 60 80 100 120 140 160 180 200 220 240 260 280 300
D—CHOAc
HC—OMe
118
MeO—CH
189
AcO—CH
CH2OAc

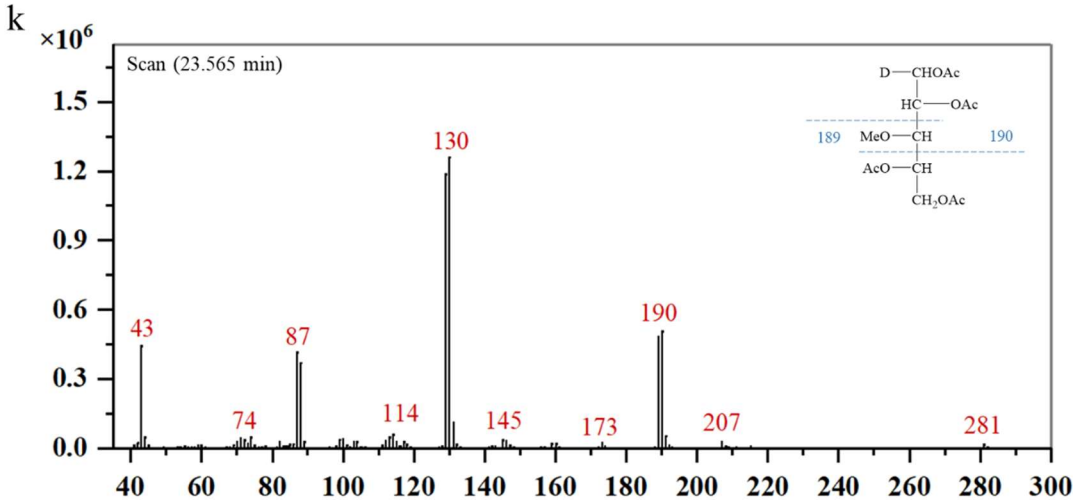
i


×10^6
Scan (19.557 min)
1.5
1.2
0.9
0.6
0.3
0.0
43
71
86
101
118
129
143
161
174
207
234
281
40 60 80 100 120 140 160 180 200 220 240 260 280 300
D—CHOAc
277
HC—OMe
118
AcO—CH
161
CH—OMe
234
CH—OAc
CH2OMe

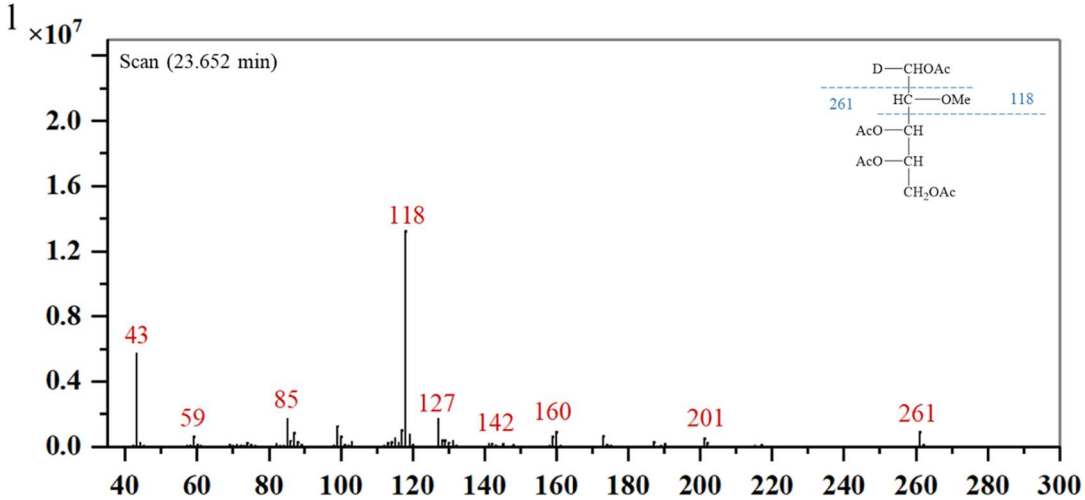
j


×10^6
Scan (22.550 min)
D—CHOAc
HC—OMe
MeO—CH
CH—OAc
CH—OAc
CH2OMe
118
233
43
59
87
99
118
129
142
162
173
207
233
281

k


×10^6
Scan (23.565 min)
D—CHOAc
HC—OAc
189
MeO—CH
190
AcO—CH
CH2OAc
130
190
43
74
87
114
145
173
207
281

l


×10^7
Scan (23.652 min)
D—CHOAc
261
HC—OMe
118
AcO—CH
AcO—CH
CH2OAc
118
43
59
85
127
142
160
201
261

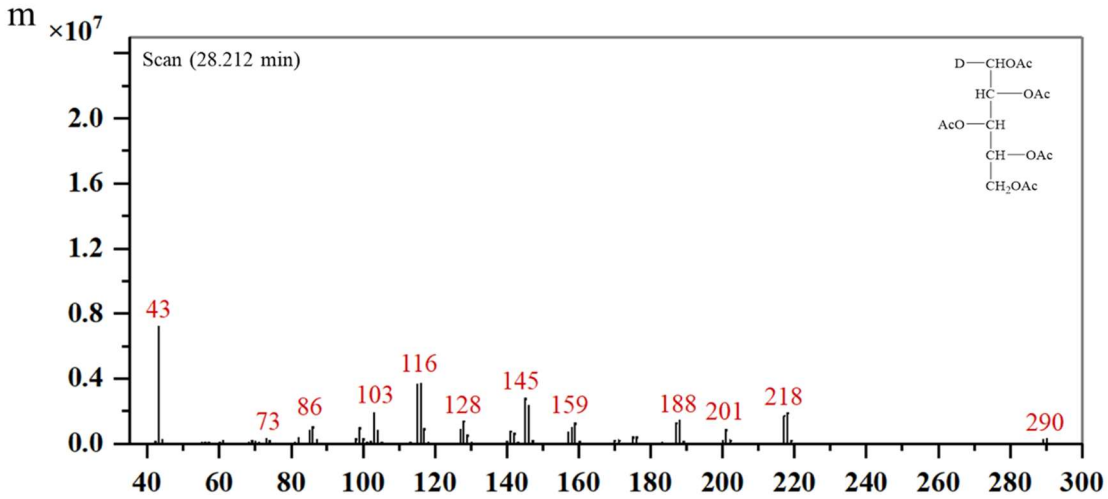


Figure S3. The results of methylation analysis. (**a**) Total ion chromatography of the PMAAs derivatives; (**b**–**m**) mass fragments of each linkage pattern: (**b**) 1,4-di-*O*-acetyl-2,3,5-tri-*O*-methyl arabinitol; (**c**) 1,5-di-*O*-acetyl-2,3,4-tri-*O*-methyl xylitol; (**d**) 1,2,4-tri-*O*-acetyl-3,5-di-*O*-methyl arabinitol; (**e**) 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methyl glucitol; (**f**) 1,3,4-tri-*O*-acetyl-2,5-di-*O*-methyl arabinitol; (**g**) 1,4,5-tri-*O*-acetyl-2,3-di-*O*-methyl arabinitol; (**h**) 1,4,5-tri-*O*-acetyl-2,3-di-*O*-methyl xylitol; (**i**) 1,3,5-tri-*O*-acetyl-2,4,6-tri-*O*-methyl glucitol; (**j**) 1,4,5-tri-*O*-acetyl-2,3,6-tri-*O*-methyl glucitol; (**k**) 1,2,4,5-tera-*O*-acetyl-3-*O*-methyl xylitol; (**l**) 1,3,4,5-tri-*O*-acetyl-2-*O*-methyl xylitol; (**m**): 1,2,3,4,5-penta-*O*-acetyl-xylitol. The PMAAs were derived from individual sugars, e.g., 1,5-di-*O*-acetyl-2,3,4-tri-*O*-methyl xylitol means that xylose was methylated at the *O*-2,3,4 sites and acetyled at the *O*-1,5 sites, which indicates that the corresponding linkage pattern was Xyl*p*-(1→.

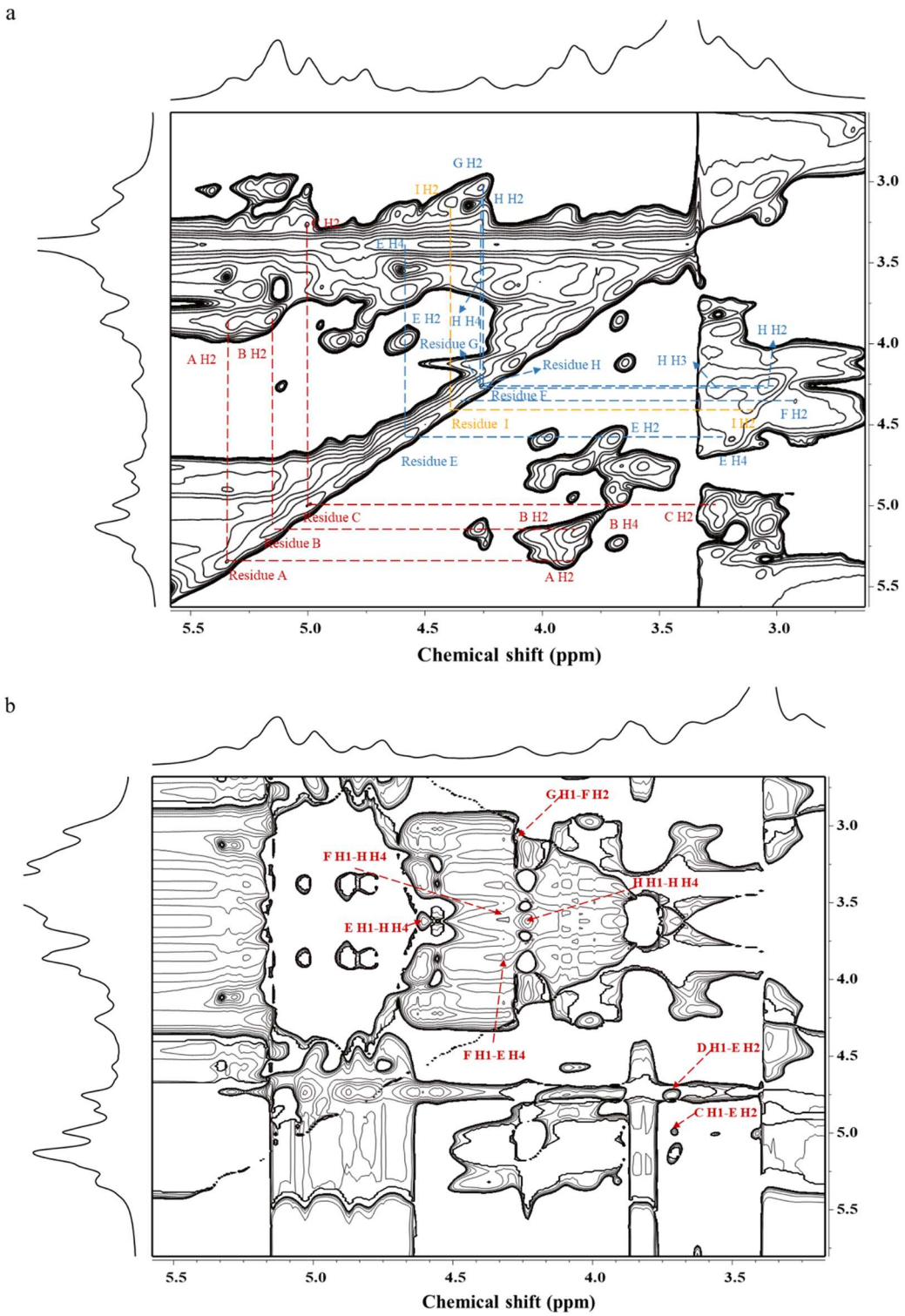


Figure S4. NMR spectra of HBAX-60: (**a**) TOCSY NMR spectrum; (**b**) NOESY NMR spectrum.