Supplemental Materials for

Mulinane and Azorellane Diterpenoid Biomarkers by GC-MS from a Representative Apiaceae (Umbelliferae) Species of the Andes

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Contents:

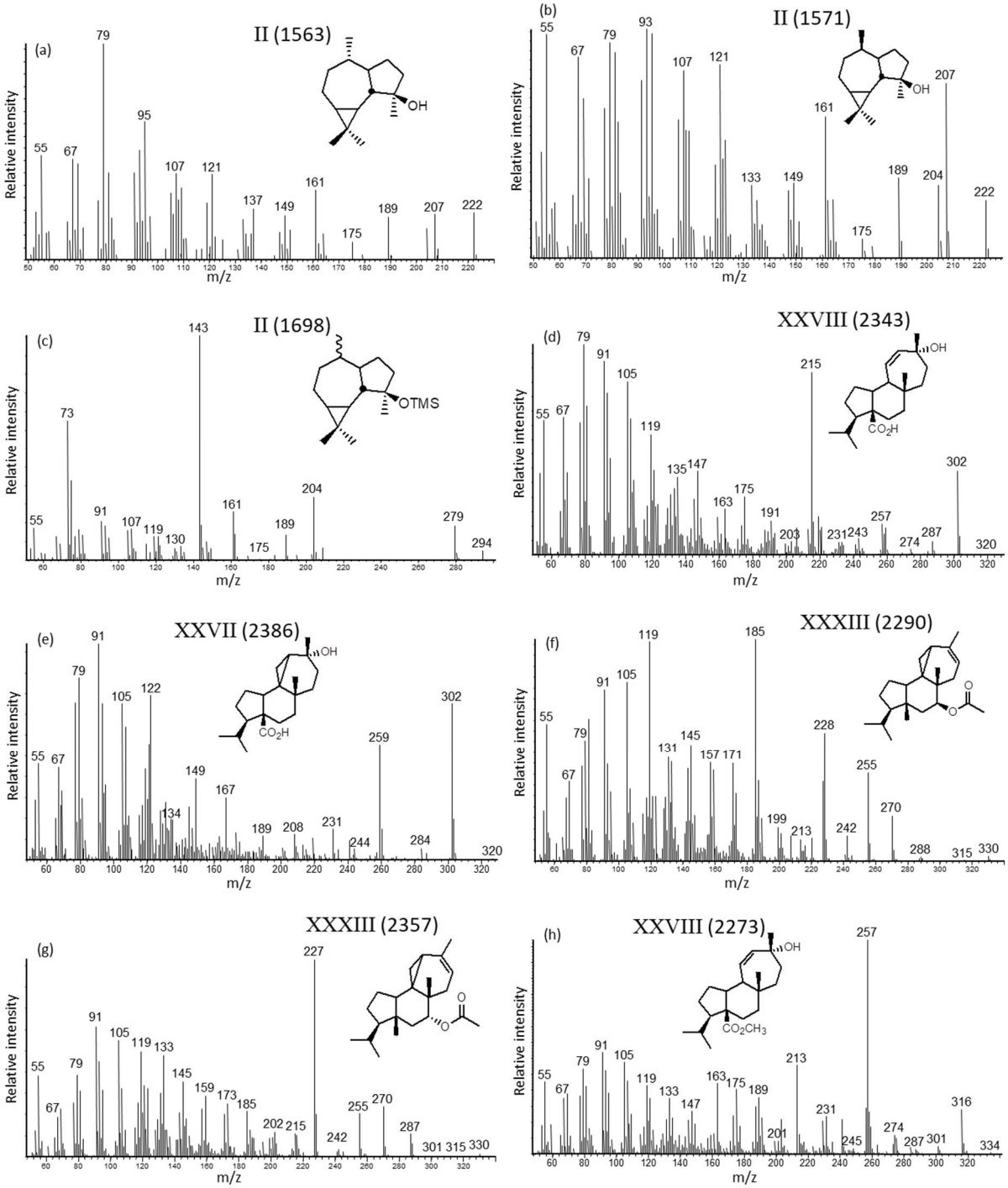
Standards

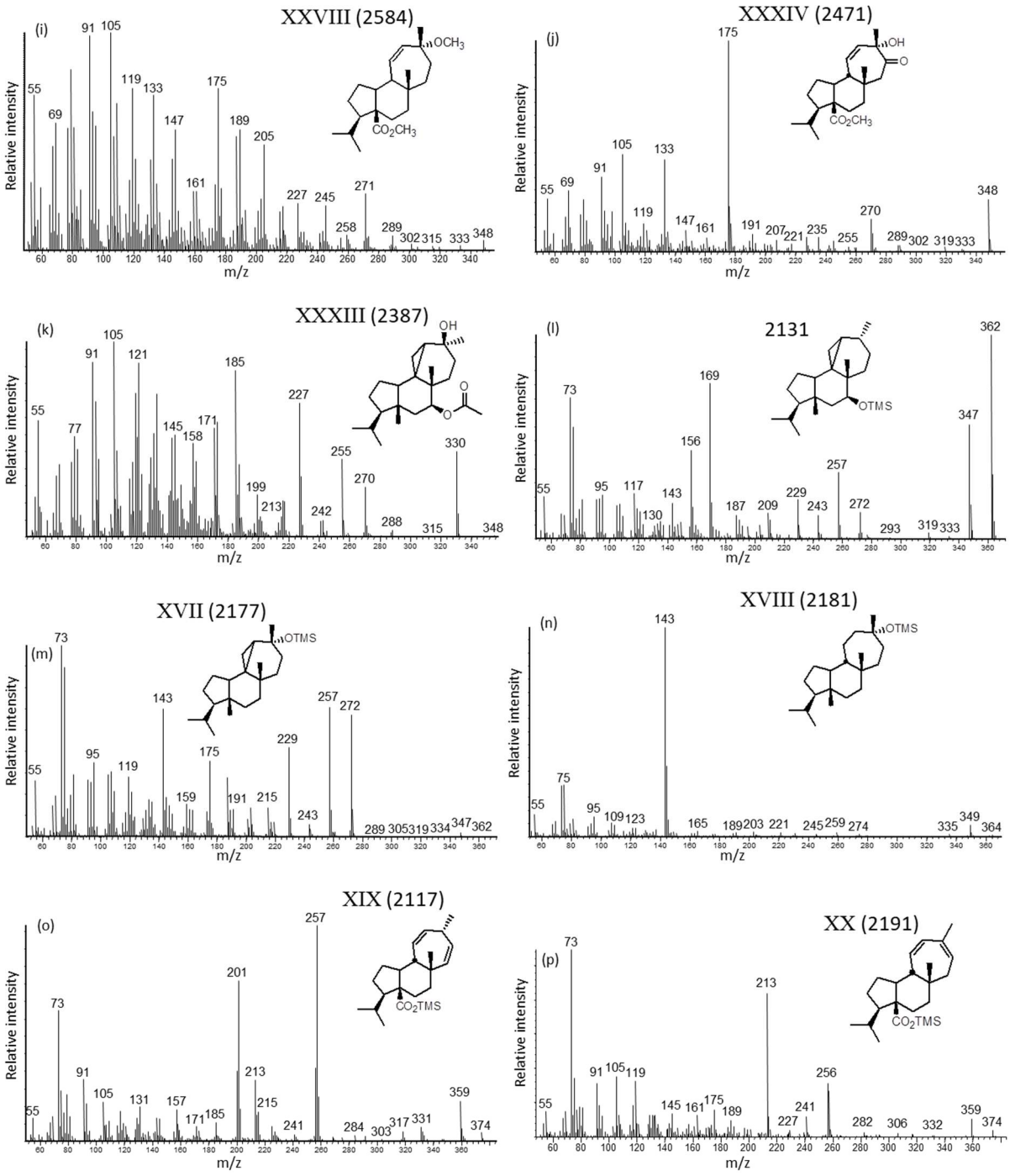
The mass spectra of primary, secondary (hydrogenated) and surrogate standards are collected in Figure SM-1. The following standard compounds were not detected in the resin sample of this report, but are provided for future reference: 13α-hydroxy-14-oxomulin-11-en-20-oic acid (Fig. SM-1j,w,z), 15α-acetoxymulina-11,13-dien-20-oic acid (Fig. SM-1x), 7β,13α-dihydroxymulin-11-ene (Fig. SM-1s), and 18-acetoxymulina-11,13-dien-16,20-dioic acid (Fig. SM-1aa).

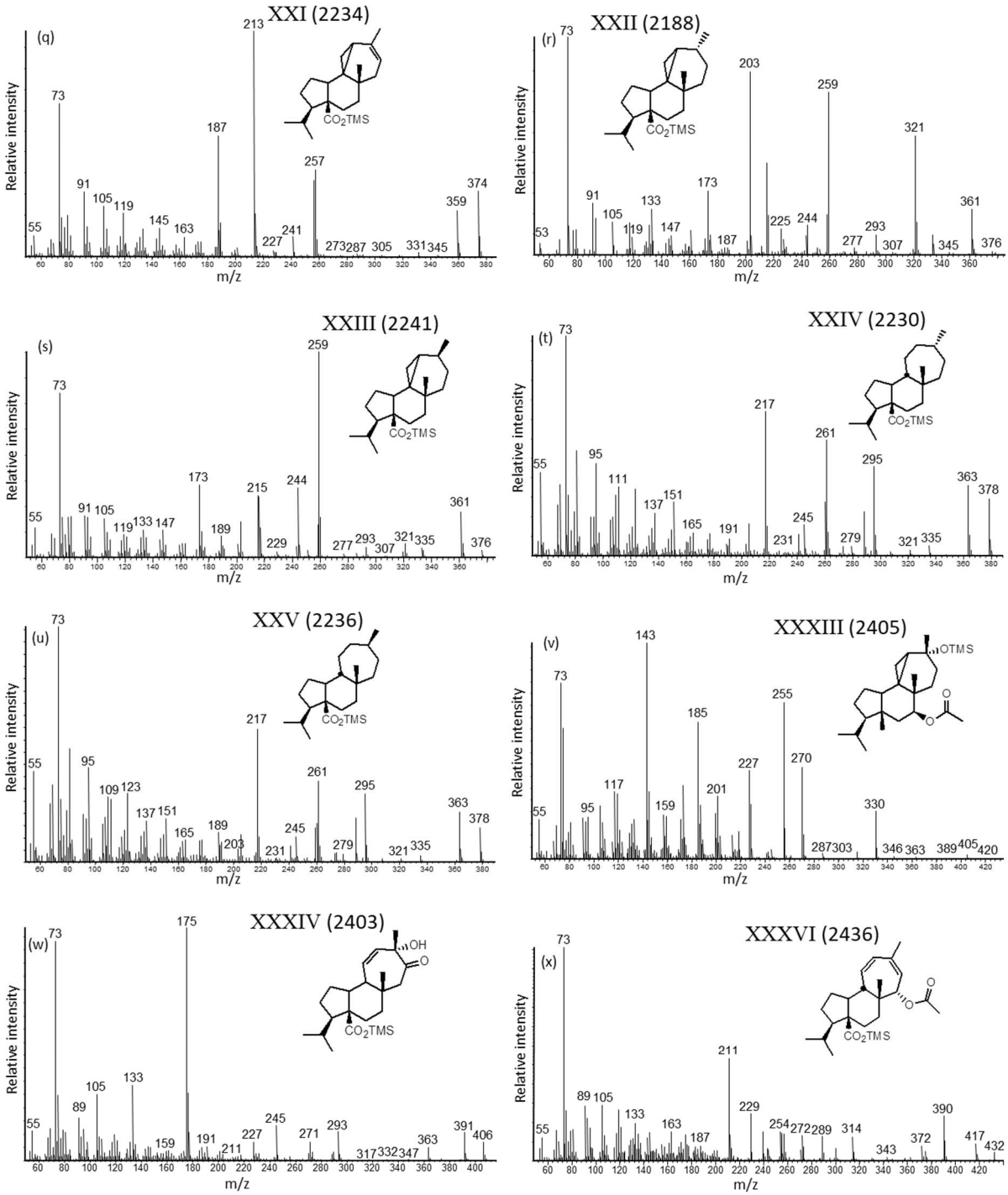
Figure SM-1. Mass spectra of derivatives, related standards and unknown compounds in *A. compacta* resins. The KI values relative to *n*-alkanes on a DB-5 column are given in parentheses on the mass spectra:

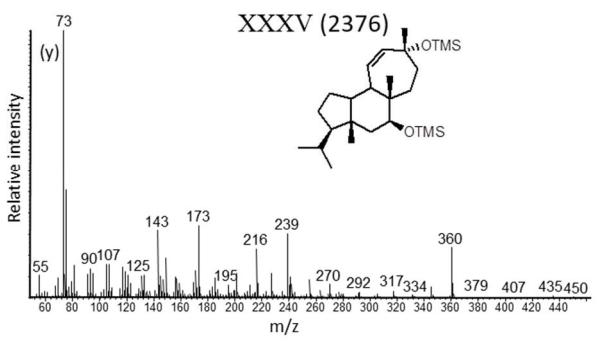
(a) α-spathulanol (II),
(b) β-spathulanol (II),
(c) spathulanol-TMS (II),
(d) mulinolic acid (XXVIII, standard),
(e) 13α-hydroxyazorellan-20-oic acid (standard, with XXVII),
(f) 7β-acetoxyazorell-13-ene (interpreted based on XXXIII),
(g) 7α-acetoxyazorell-13-ene (interpreted based on XXXIII),
(h) methyl mulinolate (XXVIII, standard),

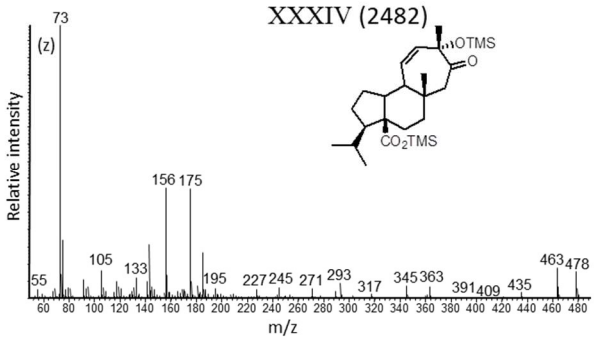
(i) methyl 13α-methoxymulin-11-en-20-oate (XXVIII, standard),
(j) methyl 13α-hydroxy-14-oxomulin-11-en-20-oate (XXXIV, standard),
(k) 13-*epi*-azorellanol (XXXIII),
(l) 7β-hydroxyazorellane-TMS,
(m) 13α-hydroxyazorellane-TMS (XVII),
(n) 13α-hydroxymulinane-TMS (XVIII),
(o) 13β(H)-mulina-11,14-dien-20-oic acid-TMS (XIX, standard),
(p) mulina-11,13-dien-20-oic acid-TMS (XX, standard),
(q) azorell-13-en-20-oic acid-TMS (XXI, standard),
(r) 13β(H)-azorellan-20-oic acid-TMS (XXII),
(s) 13α(H)-azorellan-20-oic acid-TMS (XXIII),
(t) 13β(H)-mulinan-20-oic acid-TMS (XXIV, standard),
(u) 13α(H)-mulinan-20-oic acid-TMS (XXV, standard),
(v) azorellanol-TMS (XXXIII, standard),
(w) 13α-hydroxy-14-oxomulin-11-en-20-oic acid-20TMS (XXXIV, standard),
(x) 15α-acetoxymulina-11,13-dien-20-oic acid-TMS (XXXVI, standard),
(y) 7β,13α-dihydroxymulin-11-ene-diTMS (XXXV, standard),
(z) 13α-hydroxy-14-oxomulin-11-en-20-oic acid-diTMS (XXXIV, standard),
(aa) 18-acetoxymulina-11,13-dien-16,20-dioic acid-diTMS (XXXVII, standard),
(bb) unknown $C_{20}H_{34}$,
(cc) unknown $C_{20}H_{32}$,
(dd) unknown $C_{20}H_{32}$, and
(ee) unknown $C_{20}H_{32}$.

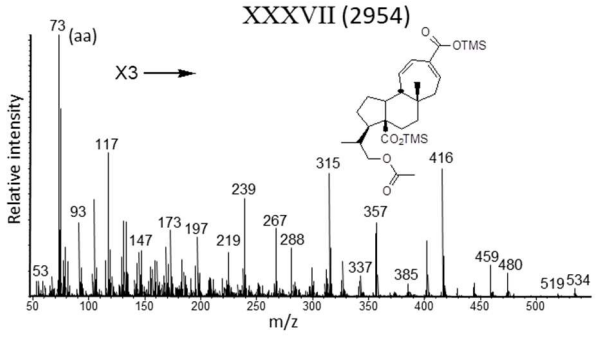

(a)
II (1563)
OH
79
95
55
67
107
121
137
149
161
175
189
207
222
Relative intensity
m/z
(b)
II (1571)
OH
55
67
79
93
107
121
133
149
161
175
189
204
207
222
Relative intensity
m/z
(c)
II (1698)
OTMS
143
73
55
91
107
119
130
161
175
189
204
279
294
Relative intensity
m/z
(d)
XXVIII (2343)
OH
CO2H
79
91
105
55
67
119
135
147
163
175
191
203
215
231
243
257
274
287
302
320
Relative intensity
m/z
(e)
XXVII (2386)
OH
CO2H
91
79
105
122
55
67
149
167
134
189
208
231
244
259
284
302
320
Relative intensity
m/z
(f)
XXXIII (2290)
O
O
119
185
91
105
55
79
67
131
145
157
171
199
213
228
242
255
270
288
315
330
Relative intensity
m/z
(g)
XXXIII (2357)
O
O
227
91
105
119
133
55
79
145
67
159
173
185
202
215
242
255
270
287
301
315
330
Relative intensity
m/z
(h)
XXVIII (2273)
OH
CO2CH3
257
79
91
105
55
67
119
133
147
163
175
189
201
213
231
245
274
287
301
316
334
Relative intensity
m/z

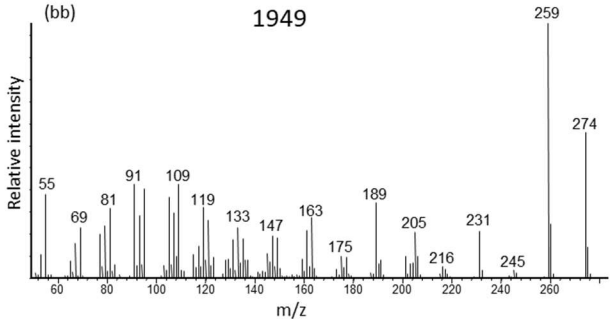

XXVIII (2584)
(i)
Relative intensity
m/z
XXXIV (2471)
(j)
XXXIII (2387)
(k)
2131
(l)
XVII (2177)
(m)
XVIII (2181)
(n)
XIX (2117)
(o)
XX (2191)
(p)

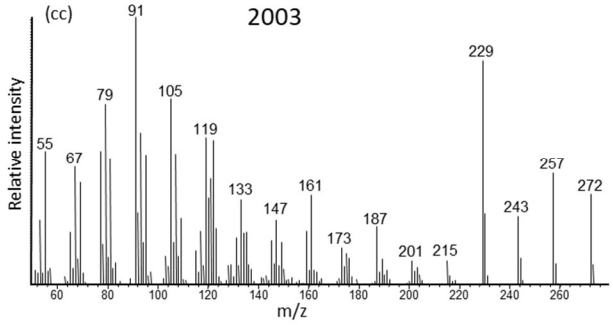

XXI (2234)
(q)
Relative intensity
m/z
CO2TMS
XXII (2188)
(r)
XXIII (2241)
(s)
XXIV (2230)
(t)
XXV (2236)
(u)
XXXIII (2405)
(v)
OTMS
XXXIV (2403)
(w)
OH
XXXVI (2436)
(x)

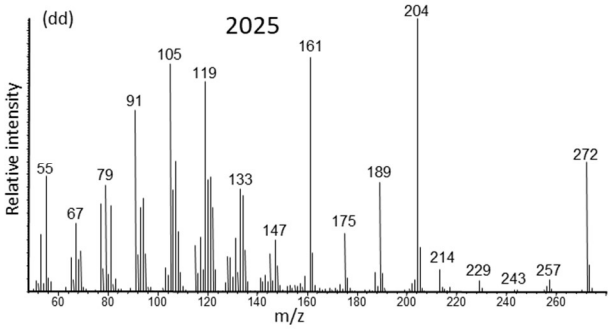

XXXV (2376)
(y)
OTMS
OTMS
Relative intensity
m/z

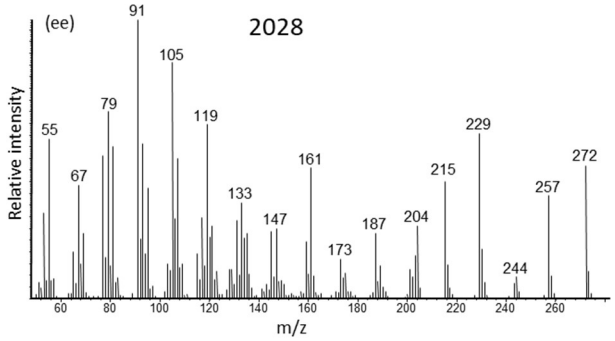

XXXIV (2482)
(z)
OTMS
O
CO2TMS
Relative intensity
m/z


XXXVII (2954)
(aa)
X3
OTMS
CO2TMS
Relative intensity
m/z


(bb)
1949
Relative intensity
m/z


(cc)
2003
Relative intensity
m/z


(dd)
2025
Relative intensity
m/z


(ee)
2028
Relative intensity
m/z

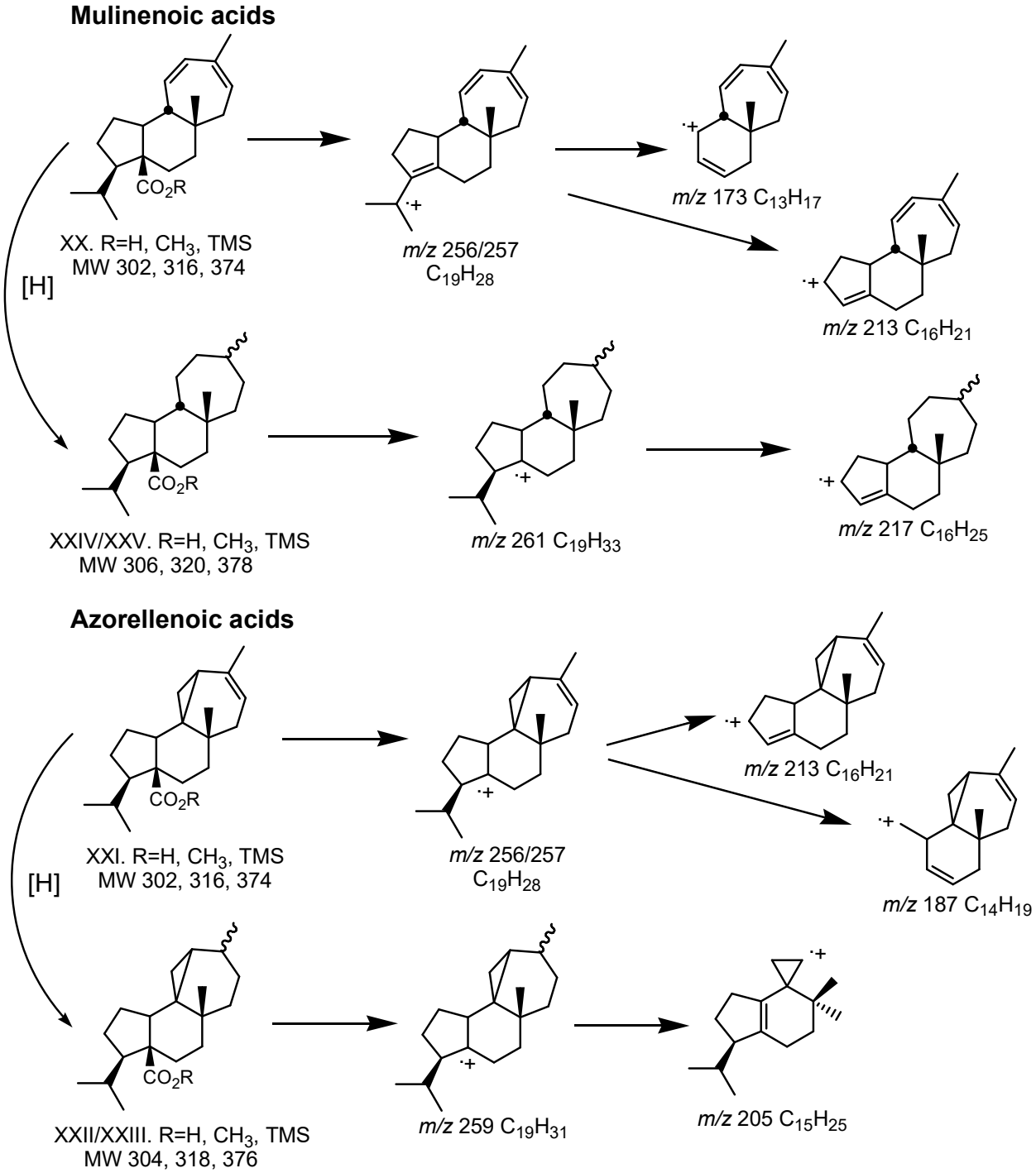


Figure SM-2a. Fragmentation scheme indicating the key ions for the mass spectra of the diterpenoid acids in *A. compacta* resin (cf. Fig. 4 in text).

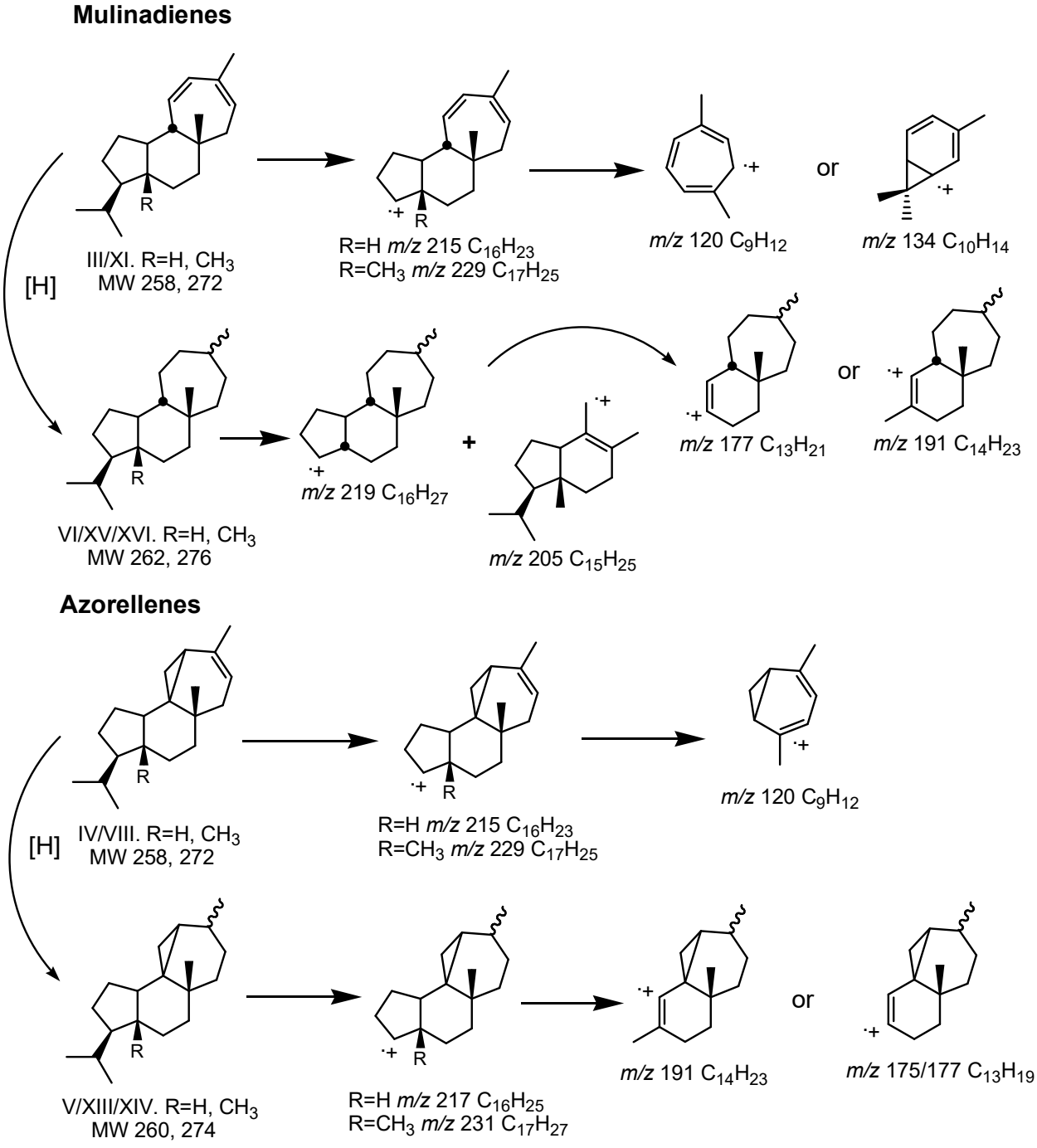


Figure SM-2b. Fragmentation scheme indicating the key ions for the mass spectra of the diterpenoid hydrocarbons in *A. compacta* resin (cf. Fig. 3 in text).