Cliff Notes on MS of derivitized (TMS) IGs

Aglycone (IG minus sugar) minus OH group

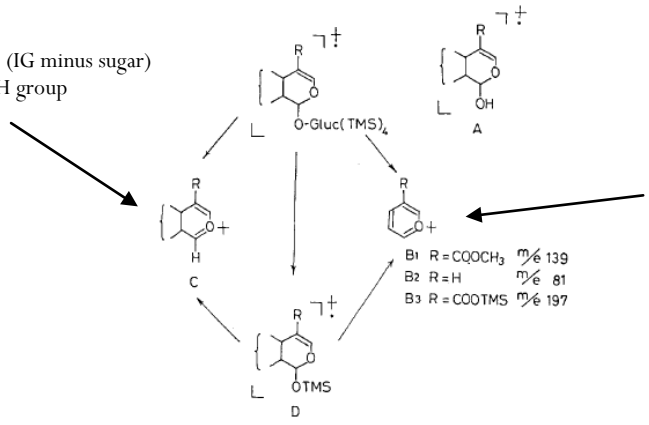


Fig. 3. Fragmentation pattern of iridoid and secoiridoid glucosides.

From Inouye 1976: Fragmentation pattern of IGs and secoIGs

Dihydropyran ring portion

Characteristic peaks of IGs

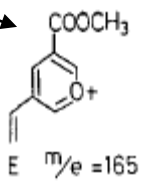
TMS=tri-methyl-silyl

1) Peaks due to sugar moiety:
    a. 361 is almost always the base peak (except for oleuropein-type iridoids), but the relative intensity of this peak in IGs is usually more intense than in glucose (supposedly!!—this is not necessarily the case in my experience)
    b. Also m/z: 271, 243, 217, 204, 191, 169, 147, 129, 103, 73 all due to sugar
    c. Also (not in Inouye), but I generally see smaller peaks at 319, 331, these are in most IGs and also sucrose, likely due to neutral losses from 361
2) One of the three (arising solely from the dihydropyran ring portion=ion B above):
    a. m/z 139 (when R is COOCH3)
    b. m/z 81 (when R is H)
    c. m/z 197 (when R is COOH [gets derivitized as COOTMS])
    d. These peaks may be very weak if there is an OH group at the C-5 position, also they are not observed at low intensity (17eV)
3) Some other fairly major peak due to the aglycone minus the C-1 hydroxy group (Ion C above) that is characteristic of each compound. This peak should correspond to Ion D minus an OTMS group (=89 mass units). May also still contain Si if there were –OH groups in the aglycone portion of IG
4) Ion D is observed at low (~17) eV, and sometimes at high (~70) eV, but intensity is much less at high eV. Ion D contains the TMS group, so you should see prominent A+2 peaks due to Si isotopic abundances

Characteristic peaks of secoIGs:

1) Should have all of the characteristic sugar peaks, plus the Ion C peak described above.
2) For those compounds in sweroside group (containing a lactone or lactame ring b/t positions 7 and 11), Ion C is the *only major* peak that results from aglucone. NO PEAKS AT 139, 81, 197 FROM ION B!!!!!
3) At low intensity (17 eV), all secoIGs have prominent peaks for Ions C + D
4) For morroniside, peak B was prominent @ 139
5) For secologanin, there is also a prominent peak for Ion E @ m/z 165 (formed by rearrangement)
6) For oleuropein-type IGs (have ethylidene or acetoxy-ethylidene side chain), sugar peaks are at low intensity, there are no peaks corresponding to Ion B, and you see additional peaks at m/z 193, 281, 167, and 165; also a low intensity peak @ m/z 225.

Lactone group=closed ring of 2 or more C with an O at one of the ring positions and also a ketone (C=O) at one of the positions. Lactam is the same but with N in the ring instead of the O.



So…to calculate what Ion C would be for any given IG:

1) Using loganin as an example:
    a. Determine MW of IG
        i. Loganin=C17H26O10, so MW=390
    b. Determine MW of TMS derivative
        i. For all –OH groups, the –H is replaced with –C3H9Si
        ii. So add 72 to the MW for each –OH group in the molecule
        iii. For loganin, the total MW of TMS derivative is 750
    c. In the formation of Ion C, the sugar portion is lost
        i. Since the sugar portion is derivitized, you need to figure what the MW of that portion will be
        ii. Start with C6H11O6 (one typical glucose H is lost in bonding w/ aglycone)
        iii. Derivitized that is C18H43O6Si4
        iv. So the MW of the lost sugar portion is **467,** this will apply to all IGs
    d. Subtract the MW of the lost portion from the MW of the TMS derivative
        i. For loganin, 750-467=**283**
2) For 7-ketologanin (reported from Lm in Ikeshiro 1992)
    a. C17H24O10, MW=388, 4 OH groups
    b. 388 + (72*4)=676
    c. 676-467=209
3) For kingiside
    a. C17H24O11, MW=404, 4 OH groups
    b. 404 + (72*4)= 692
    c. 692-467=225
4) For secoxyloganin
    a. C17H24O11, MW=404, 5OH groups
    b. 404+(72*5) =764
    c. 764-467=297
5) For 8-epi-loganin
    a. $C_{17}H_{26}O_{10}$, MW=390, 5 –OH groups
    b. 390 + (72*5)=750
    c. 750-467=283
6) For morroniside
    a. $C_{17}H_{26}O_{11}$; MW=406; 5 OH groups
    b. 406+ (72*5)=766
    c. 766-467=299, formula should be C18H43O6Si4
7) For secologanin
    a. $C_{17}H_{24}O_{10}$; MW=388, 5OH groups
    b. 388+(72*5)=748
    c. 748-467=281
8) For secologanin dimethyl acetal
    a. C19H30O11; MW=434; 4 OH groups
    b. 434+ (72*4)=722
    c. 722-467=255
9) For sweroside
    a. $C_{16}H_{22}O_9$; MW=358; 4 OH groups
    b. 358 + (72*4)=646
    c. 646-467=179
10) For loganic acid
    a. $C_{16}H_{24}O_{10}$, MW=376, 6OH groups

RPDB rule: For composition CxHyNzOn
RPDB=x – 1/2 y + 1/2 z + 1
-This number cannot be <-0.5
-Integers for odd-electron ions, end in .5 for even-electron ions
More general case
$A_yB_nC_zD_x$, where
A = H, F, Cl, Br,I;
B = O, S;
C = N, P;
D = C, Si

b. 376 + (72*6) = 808

c. 808-467=341

11) For secologanic acid

a. $C_{16}H_{22}O_{10}$, MW=374, 5OH groups

b. 374+ (72*5)=734

c. 734-467=267

12) For 7-deoxyloganic acid

a.

Interpretation of Unknowns from Arnold Arb samples

1) Unknown A: prominent peak @ 301, this could be Ion C
    a. Peak intensity @ 301=641, @302=72, nothing @303
    b. No A+2 peak indicates no Si
    c. 302 is 11.23% of 301, indicates C10
    d. Elemental composition calculator gave only two options: C10H37O9 or C10H21O10
    e. For option 1, RPDB=-7.5, not possible!
    f. For option 2, RPDB=0.5, this is possible!
    g. Formula is likely C10H21O10 for Ion C
    h. Plus sugar moiety, C6H11O6
    i. So total IG formula is: **C16H32O16**, R is COOCH3, other side chains of Ion C will contain C3H14O7
2) Unknown Y: peak @ 255 could be Ion C
    a. Peak intensity @ 255=91, peak intensity @255.2=39, this can't be due to A+1 isotope abundance, must be interference or background, so I am not sure…
3) Unknown C: peak @ 359 could be Ion C (or this could be due to losses from 361, but I haven't seen this in other spectra so doesn't seem likely
    a. Peak intensity @ 359=1086, @ 360=173, impossible to tell A+2 since 361 is so large.
    b. 360 is 15.9% of 359, indicates C14 (unless there is also Si, then could be C9)
    c. Small peak @ 197 could be Ion B
4) Unknown D
    a. No likely candidates for Ion C—peaks @ 341 and 251, but neither has A+1 peak
    b. No peaks @ 139, 81, or 197 indicating Ion B
5) Unknown SS
    a. Large peak @ 329 could be Ion C; Int. @ 329=2870, @330=642, @331=533
        i. A+2 intensity is 18.6%, complicated by the fact that there is likely some interference, often see 331 peak due to sugar moiety; so not sure if there is Si or not
        ii. Would guess there is some A+2 contribution from 329, since the typical ratios of 331/332/333 are off from what they are in other spectra with 331 peak—332 is too high and 333 is too low, so maybe the isotopic peaks from 329 are contributing to both 331 (A+2) and 332 (A+3)—this hypothesis would require at least two Si's in the 329 Ion to get the A+3 contribution.
        iii. A+1 intensity is 22.4%, if there were two Si then 10.2% of this would be due to those. Rest would be due to C, suggesting (22.4-10.2=12.2%), so likely C11 (maybe C10?)
        iv. Elemental composition calculator suggests 6 possibilities:
            1. C11H49O4Si2; not possible RPDB rule
            2. C11H33O5Si2; not possible RPDB
            3. C11H17O6Si2; possible!
            4. C10H45O5Si2; not possible
            5. C10H29O6Si2; not possible

6. C10H13O7Si2; possible!!

v. So our two possibilities are: C11H17O6Si2 and C10H13O7Si2
   1. Both of these are within the error of the isotopic abundances
   2. However, neither of these make sense because for each of the Si atoms you would need C3H9 for the tri-methyl-silyl groups; so you would need at least C6H18 just for that part.

vi. Re-do with only one Si atom, in this case the A+1 contribution from Si is only 5.1%, so you could have 17.6% contribution from C, suggesting up to C16 composition suggests 6 possibilities:
   1. C16H49O2Si; not possible!
   2. C16H33O3Si; possible!
   3. C16H17O4Si; possible!
   4. C15H45O3Si; not possible!
   5. C15H29O4Si; possible!
   6. C15H13O5Si; possible

For isotope data, McLafferty suggests a rule of thumb for error of intensity estimates to be +/- 10% relative or 0.2 absolute, whichever is greater.

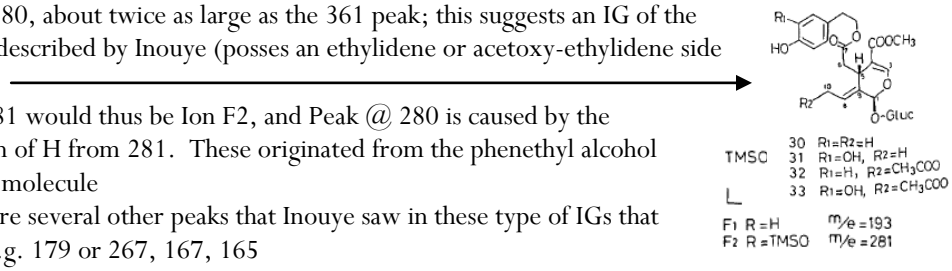
vii. Four possibilities are: C16H33O3Si ; C16H17O4Si ; C15H29O4Si ; C15H13O5Si
   1. Isotope calculator says A+1 for each of these should be 23.174%, 23.03%, 22.067%, 21.92%, respectively. All are within error for observed 22.4%

b. Peak @ 139 is Ion B, suggests R group is COOCH3

c. Peak @ 165, Ion E

6) Unknown TT

a. Largest peak is @ 280, about twice as large as the 361 peak; this suggests an IG of the oleuropein-type as described by Inouye (posses an ethylidene or acetoxy-ethylidene side chain). Such as:



   i. Peak @ 281 would thus be Ion F2, and Peak @ 280 is caused by the elimination of H from 281. These originated from the phenethyl alcohol portion of molecule

b. However, there were several other peaks that Inouye saw in these type of IGs that I do not see here, e.g. 179 or 267, 167, 165

c. These type of IGs do not give a peak associated with Ion B

7) Unknown F

a. Peak @ 299 is likely Ion C
   i. A+1 is 22.5%, A+2 is 9.1%
   ii. Formula of Ion C for morroniside should be C14H23O5Si, this would predict A+1 abundance of 20.94% and A+2 of 4.38%
   iii. There is also a pretty big peak at 298 so there is likely some interference.

b. Peak @ 139 is Ion B

c. Also small peaks @ 149 and 181 are consistent with published morroniside spectra—not sure what these would be though.

8) Unknown G

a. No 361 peak, also missing several other sugar peaks 271, 243, 169, many others are very small

b. Base peak is @ 345; A+1 is 34.73%, A+2 is 15%; would suggest Si4?

c. Not convinced this is an IG, will likely leave out

9) Unknown I

a. Has peak at 225 that could be Ion C, same as kingiside—these two compounds have a strong match in library searches—usually 90% match with H to I and I to H

b. Has peak @ 314 similar to Unknown H—not sure what this is?
   i. No A+2 peak, but could be below detectable limit since intensity is only 527
   ii. A+1 peak is confusing—there is a peak @ 315, intensity 41 and then @ 315.15, intensity 97

c. Has a large peak @ 139, corresponds to Ion B

d. Also a peak @ 165, corresponds to Ion E
e. Searched SciFinder for all compounds that have the same formula as kingiside (also formula predicted by aglycone @ 225), and found only 3 options—kingiside, 8-epi-kingiside, and iso-8-epi-kingiside. Can't necessarily distinguish b/t 8-epi and iso-8-epi, but 8-eip is much more common, has been reported in many plant species so this seem much more likely.

10) Unknown H
    a. Has peak @ 225 that could be Ion C (same as Unknown I)
        i. Consistent with kingiside—present in high quantities along with morroniside, and in fruits only, so it seems highly likely that this is the compound identified by Souzu and others.
    b. Has large peak @ 139, consistent with Ion B
    c. Also a peak @ 165, consistent with Ion E
    d. Shares many small peaks with Unknown I, incl. 305, 297, 236, 229, 155, 117, 89, 59, 45 (many of these in other seco-IGs also); these compounds are likely highly related—also get 90% matches between them.
11) Unknown CC
    a. Has all the sugar peaks, but 361 is very small and the base peak is 204, much larger than any other peak.
    b. No peaks corresponding to Ion B or Ion E
    c. Not convinced this is an IG
12)

Typical background peaks in Susan's data:

-m/z 8,18, 28 (larger), 32, 40, 44, 73, 75, 147, 207

-also at higher temps (towards end of 48 min IG run), I get lots more of the above, plus major ones at 221, 249, 267, 281 (larger), 341, 361, 429, 503

Compound info:

7-ketologanin ($C_{17}H_{24}O_{10}$)
https://origin-scifinder.cas.org/scifinder/view/link_v1/substance.jsf?l=t7c60yhXV6s4qIK1TONqN7MY16H75Rnkxvyd6TbOdxglCsJiZFw9isQw5xtuNwIc

minus glucose(TMS4)=