Identification of aggregation pheromone of brown marmorated stink bug

by creating stereoisomeric libraries of 1-bisabolen-3-ols

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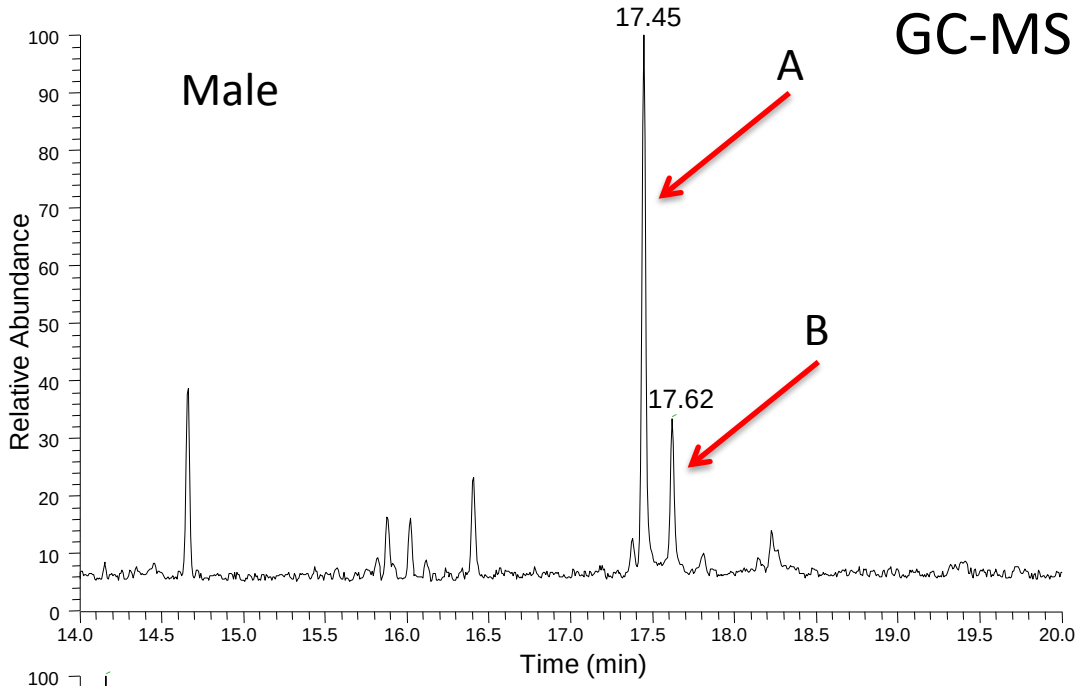
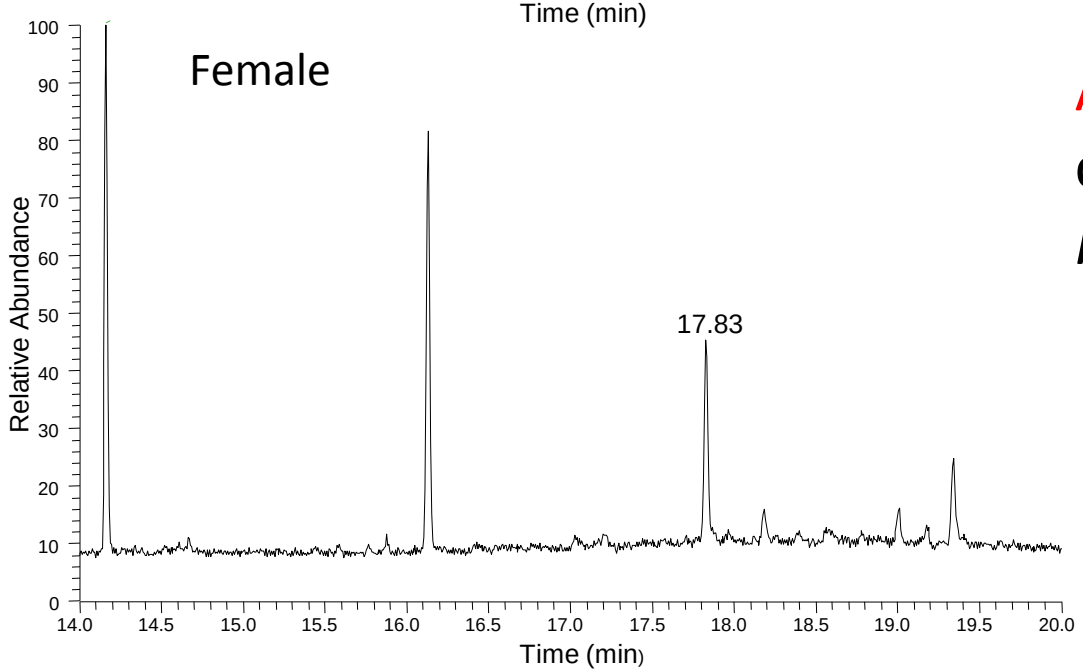
GC-MS total ion chromatograms

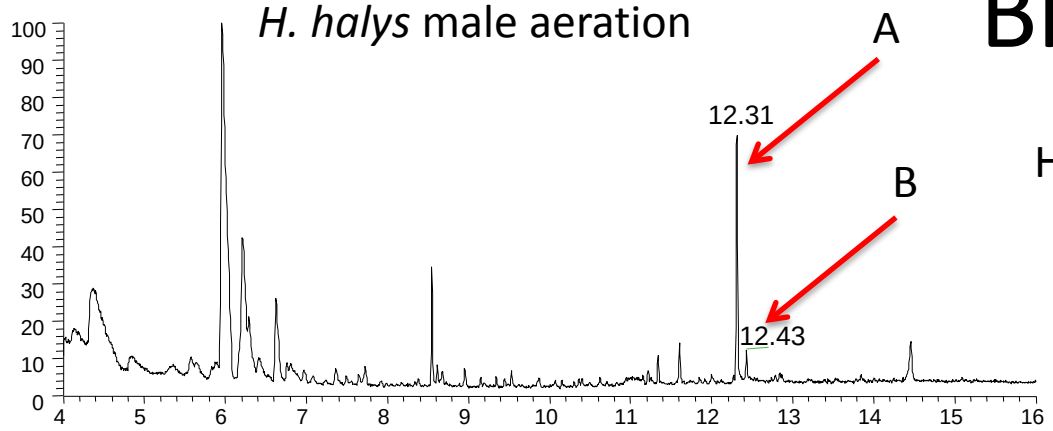
Hsiao-Yung Ho



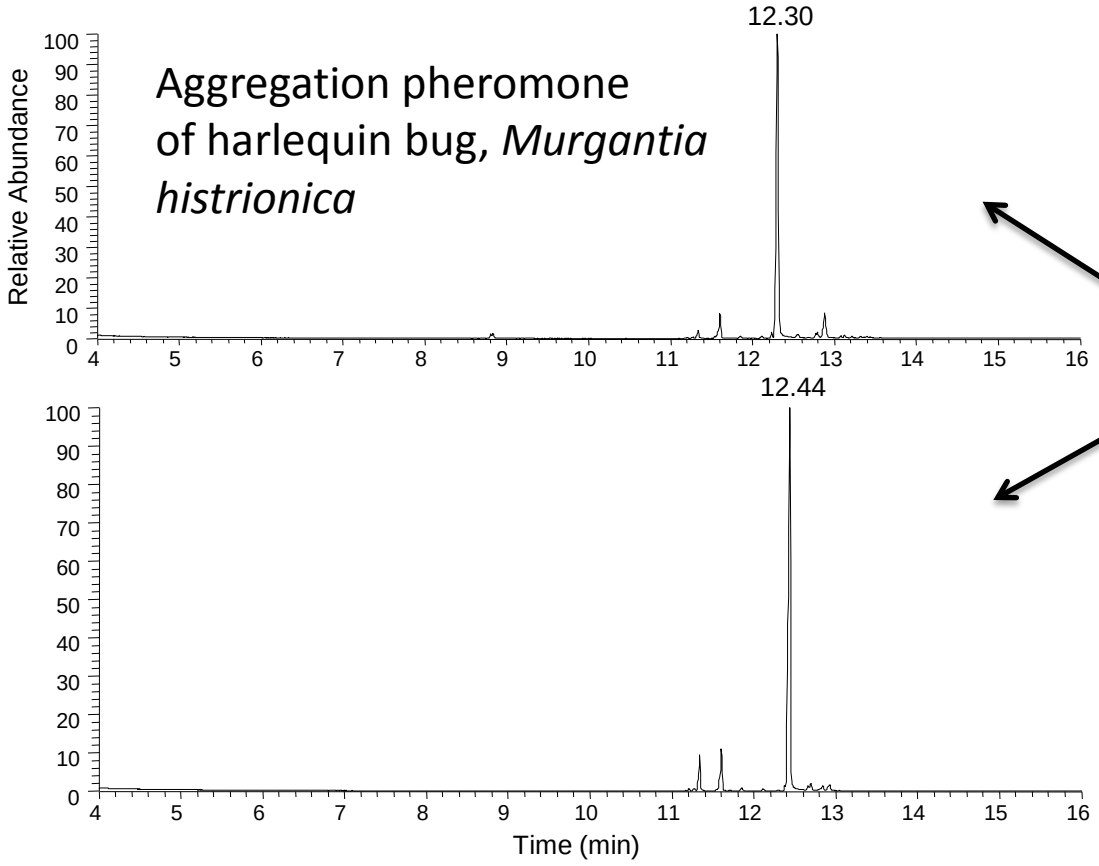


A and B are male-specific compounds not found in *H. halys* females

Breakthrough #1



Hsiao-Young Ho, 2009



Synthetic murgantiols

1,10-bisaboladien-3-ol

total 8 stereoisomers

10,11-epoxy-1-bisabolen-3-ol

total 16 stereoisomers

Dictionary of Terpenoids, v.1, 1991

Natural occurrence of 1,10-bisaboladien-3-ols and 10,11-epoxy-1-bisabolen-3-ols

- Representative 1,10-bisaboladien-3-ol (a.k.a. zingiberenol) was isolated from ginger, *Zingiber officinale*
- 1,10-Bisaboladien-3-ols were identified as rice stalk sting bug, *Tibaca limbativebtris*, pheromone
- 10,11-Epoxy-1-bisabolen-3-ol (called murgantiol) was identified as aggregation pheromone of harlequin bug, *Murgantia histrionica*
- Male brown marmorated stink bug, *Halyomorpha halys*, produce 10,11-epoxy-1-bisabolenols
- In all four studies, *absolute configurations* and *field attractiveness of pheromones have not been demonstrated*

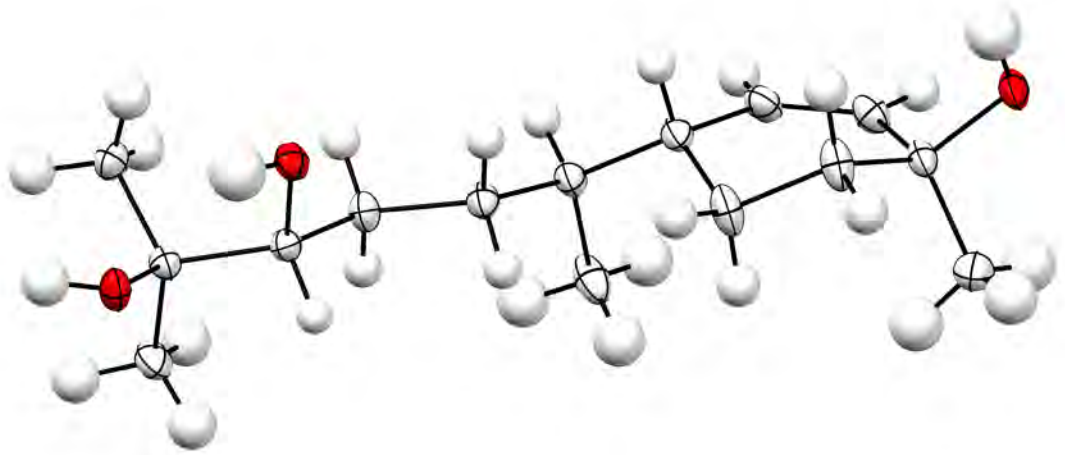
Breakthrough #2

Two stereoisomers from one reaction

Breakthrough #3

Maxime Siegler, JHU

X-Ray (Cu *K*α) structure determination of intermediate triol



Displacement ellipsoid plot of crystalline RSRS triol

Synthesis of individual stereoisomers of 10,11-epoxy-1-bisabolen-3-ol

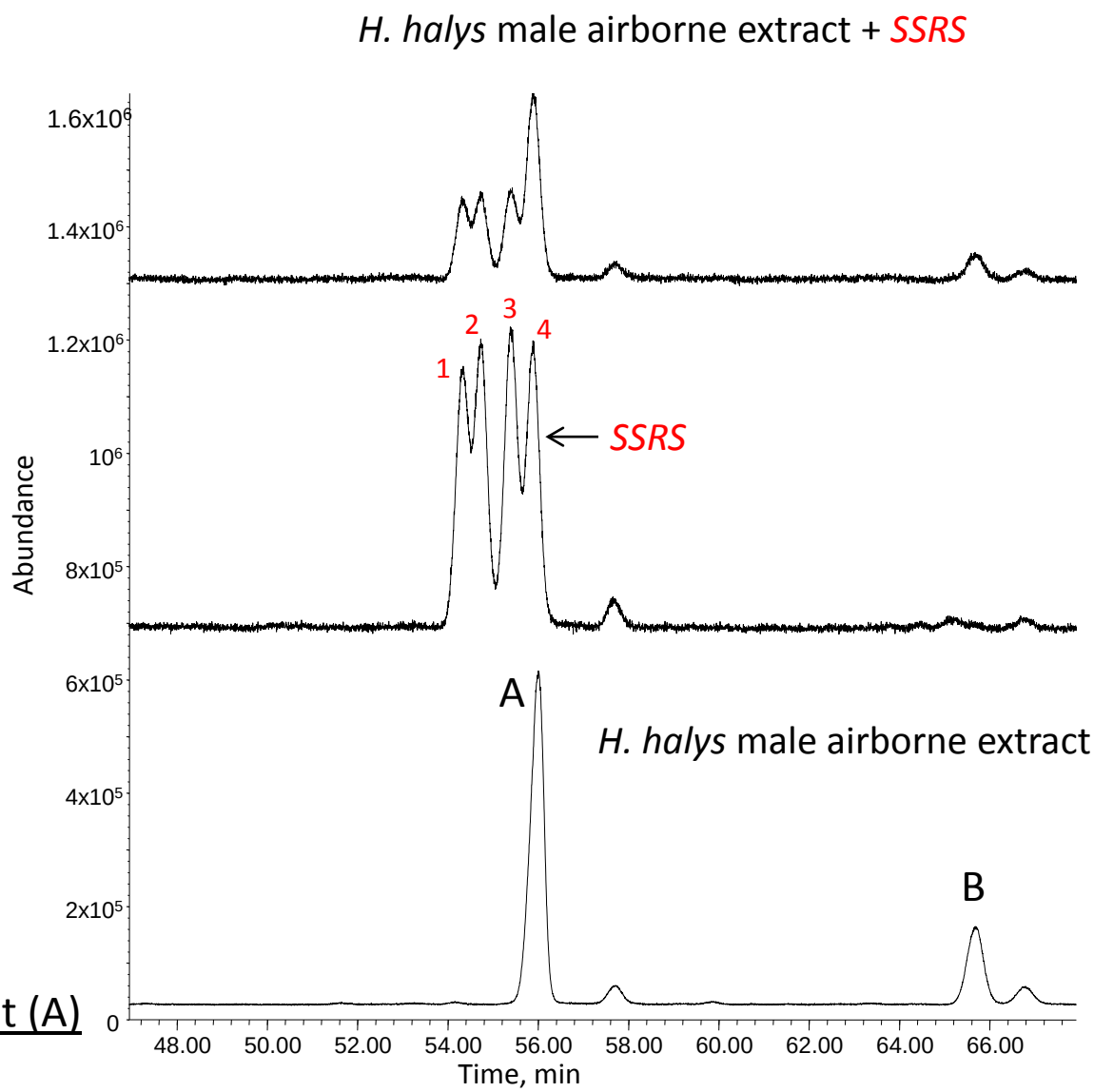
(3*S*,6*S*,7*R*,10*S*)-10,11-epoxy-1-bisabolen-3-ol, main component of brown marmorated stink bug aggregation pheromone

Synthetic work: Summary

We synthesized and streochemically characterized previously unknown:

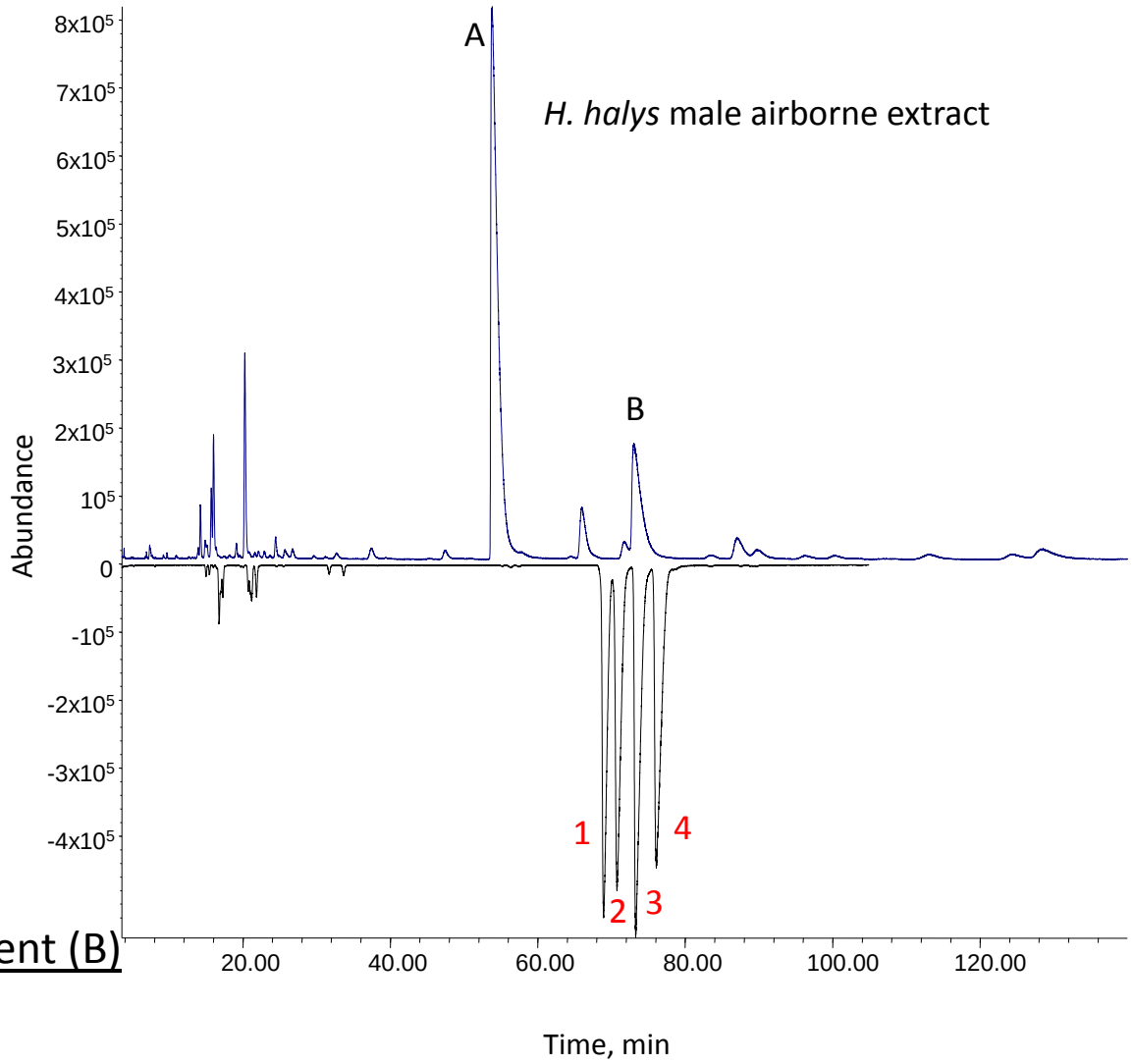
- All 8 possible stereoisomers of 1,10-bisaboladien-3-ol
- All 16 possible 1-bisabolen-3,10,11-triols
- All 16 possible 10,11-epoxy-1-bisabolen-3-ols

Breakthrough #4



BMSB main pheromone component (A) identified!

Breakthrough #5



BMSB minor pheromone component (B) identified!

Brown Marmorated Stink Bug Pheromone Identification: Summary

- Main component of BMSB aggregation pheromone (A) has been identified as (3*S*,6*S*,7*R*,10*S*)-10,11-epoxy-1-bisabolen-3-ol
- Minor component of BMSB aggregation pheromone (B) has been identified as (3*R*,6*S*,7*R*,10*S*)-10,11-epoxy-1-bisabolen-3-ol
- Availability of all 16 stereoisomers and combination of two chiral columns streamlined the assignments and bioassay confirmed the identification.

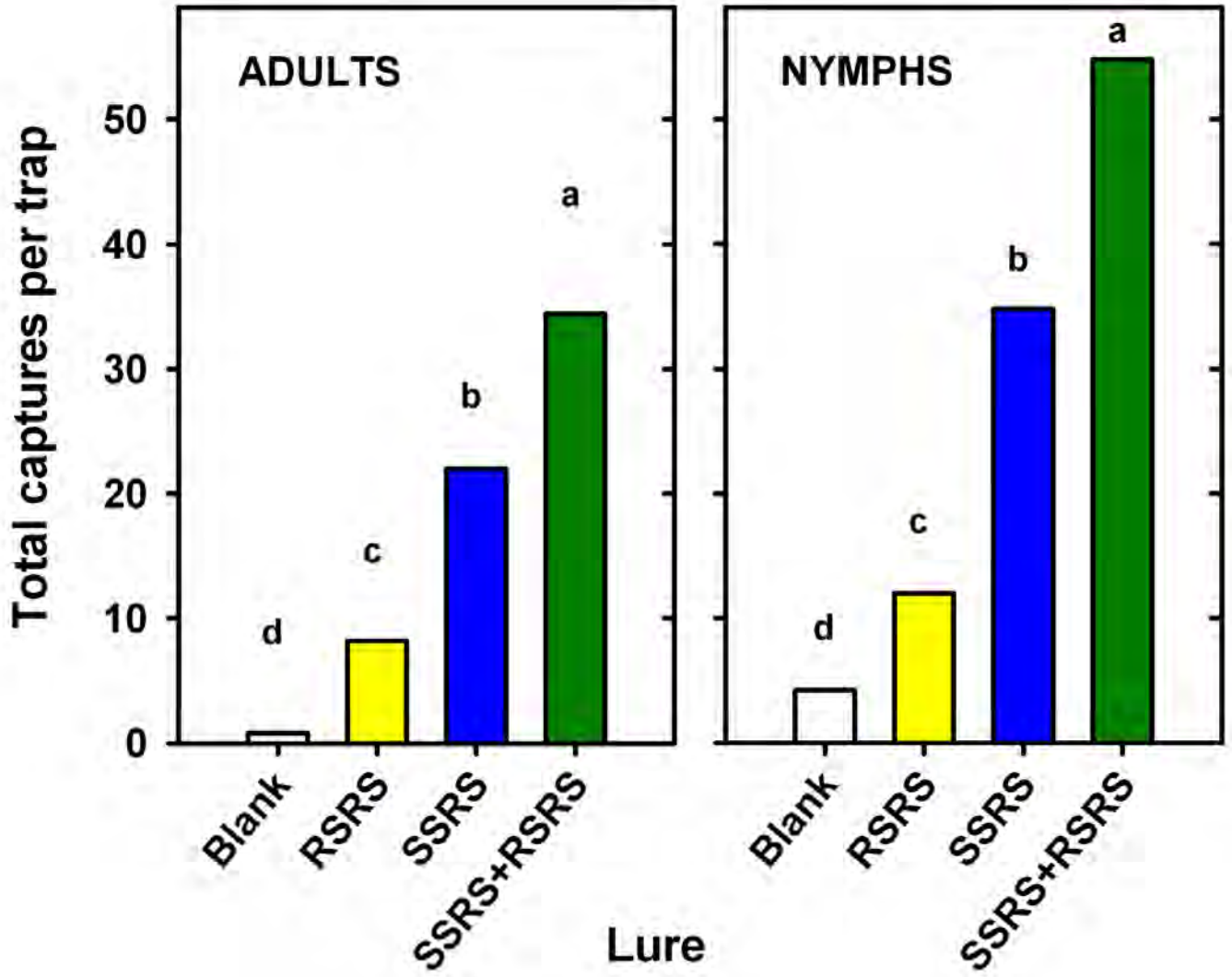
A

B

Breakthrough #6

H. halys captures in pyramid traps with pheromone components

(Don Weber)



Breakthrough #7

Trapping *H. halys* with mixed-isomer lures

(Tracy Leskey)

Treatment	Adults	Nymphs
#2 (M4)	159.0 ± 12.4 b	5.4 ± 2.5
#4 (control)	49.6 ± 14.3 b	6.2 ± 3.1
#6 (M4+Cs)	201.2 ± 23.8 b	7.8 ± 3.7
#9 (M4+Cs+220)	174.8 ± 45.9 b	6.8 ± 1.6
#10 (RM4+Rcis)	**758.4 ± 164.1a**	7.2 ± 1.8