



Click beetles and pheromones – an overview

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Wireworms, the larvae of click beetles (Coleoptera: Elateridae) are important soil-dwelling polyphagous pests all over the world.



Traditional forecast and monitoring involves labour-intensive soil sampling methods,





and to obtain wireworms from soil samples collected is time-consuming
(several days or more).

Photo L. Furlan

Pheromone-baited traps are much easier and simpler to use.

However, the pheromone composition should be identified first!



Photo M. Tóth

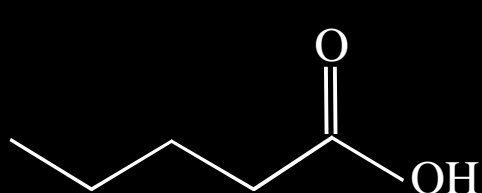
On the picture: the YF trap design specifically developed for pheromone trapping of click beetles (Furlan Inform. Fitopat. 10:49. (2004))

Pheromone structures - first identifications

The very first chemical structures elucidated from click beetles (female-produced pheromone) were organic acids



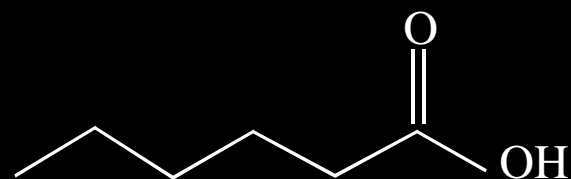
Limonius californicus
www.bugguide.net



valeric acid (pentanoic acid)

Limonius californicus

Jacobson Science 159:208
(1968)



caproic acid (hexanoic acid)

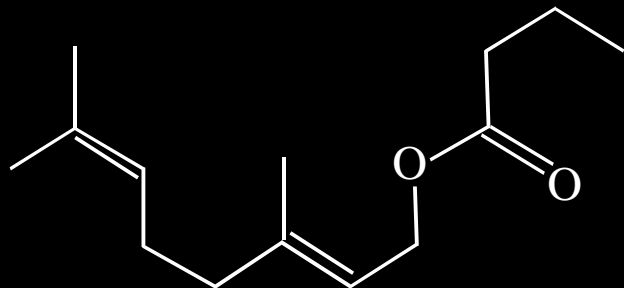
Limonius canus

Butler Environ. Entomol. 4:229
(1975)

Pheromone structures - geranyl/farnesyl esters

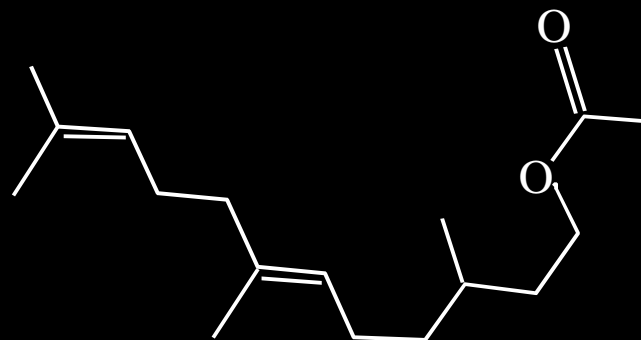
Starting from the eighties, a number of geranyl and farnesyl esters were identified mainly by scientists from the Soviet Union.

Example structures:



geranyl butyrate
[(*E*)-3,7]-dimethyl-2,6-
octadienyl butyrate]

i.e. *A. sputator*



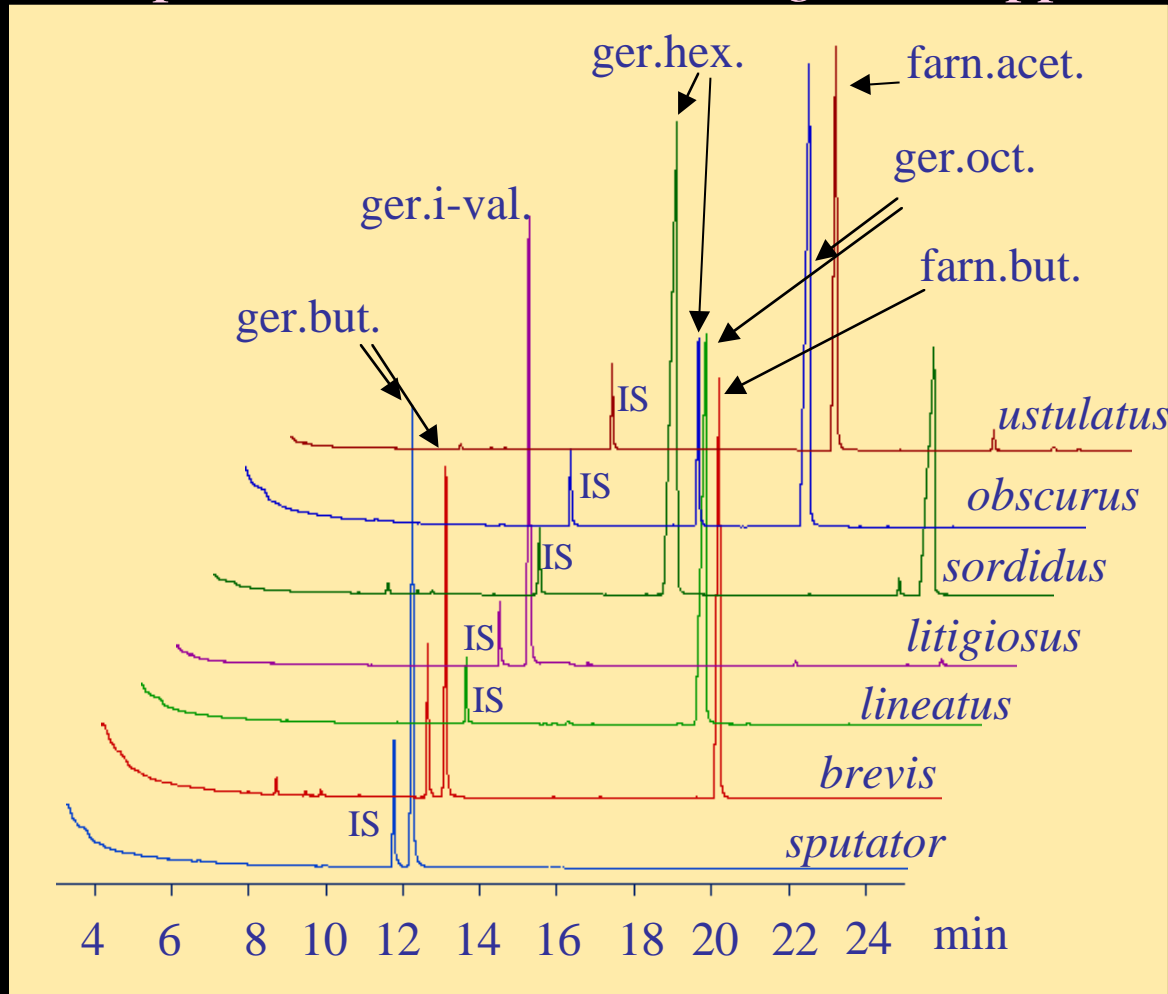
(*E,E*)-farnesyl acetate
[(*E*)-3,7,11]-trimethyl-2,6,10-
dodecatrienyl acetate]

i.e. *A. ustulatus*

First report on similar structures from: Oleschenko, 1979, cited in Kamm, Coleopt. Bull. 37:16 (1983)

Pheromone structures - geranyl/farnesyl esters

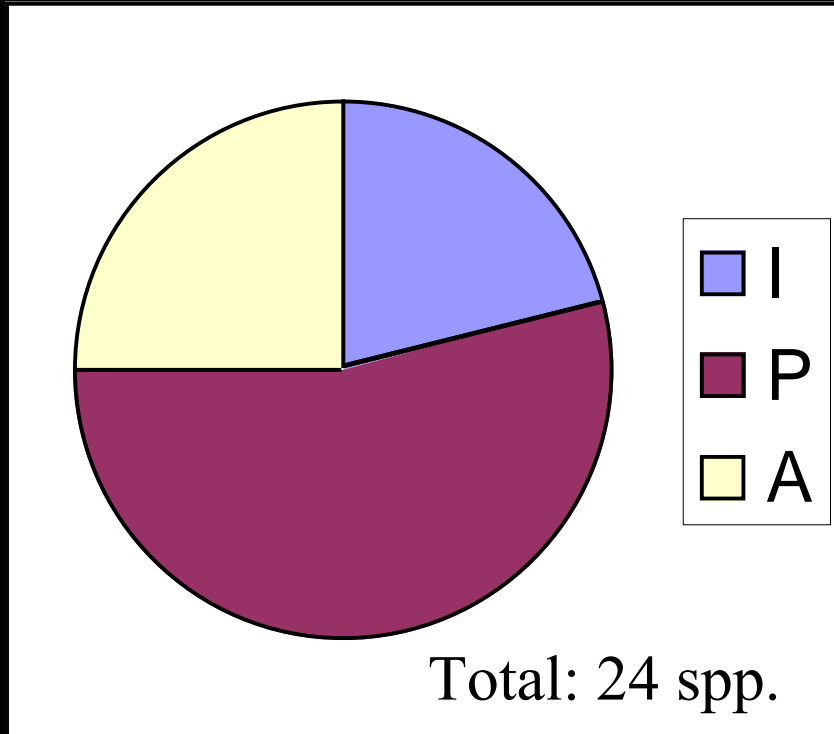
Permutations and combinations of such compounds are present in the pheromones of several *Agriotes* spp.



GC analysis of pheromone gland extracts of *Agriotes* spp. (after Tóth J. Chem. Ecol.. 28:1641 (2002) and Pest Manag. Sci. 59:1 (2003))

Pheromone structures - geranyl/farnesyl esters

Structures for many spp. were reported, however, a great part of these compounds showed no behavioral activity.



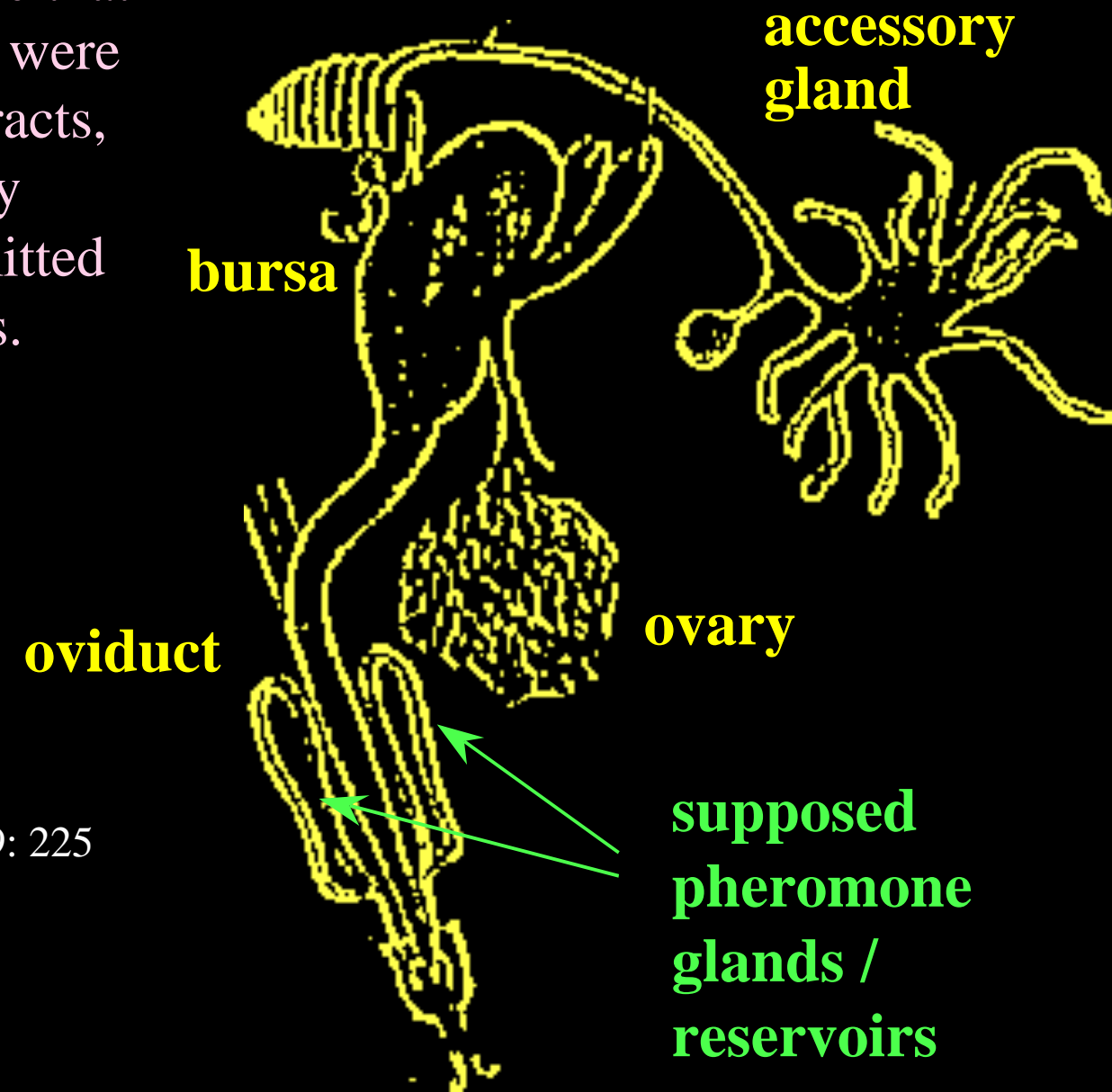
I = compound identified but no behavioral activity shown

P = compound identified, found attractive

A = synthetic compound attractive, but not known whether present in female

Pheromone structures - geranyl/farnesyl esters

One reason for this may be that most early identifications were based on direct gland extracts, which may not necessarily represent composition emitted into the air by the females.

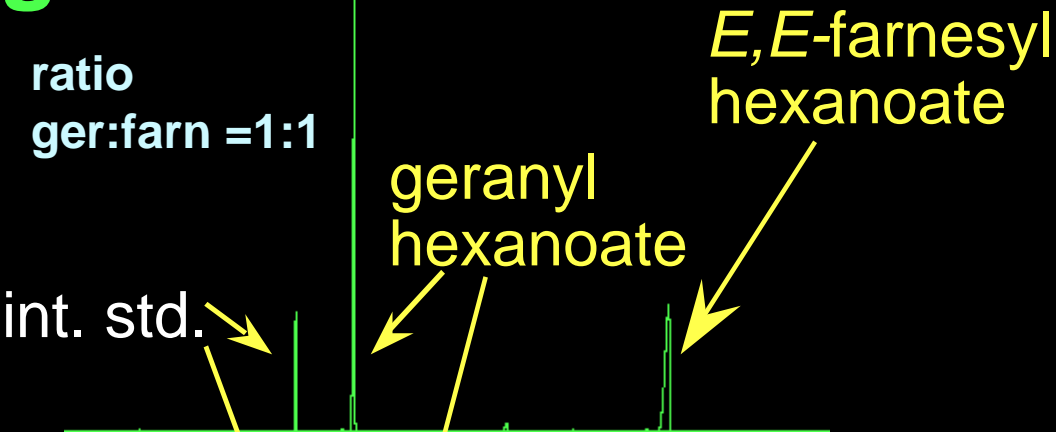


(After Ivaschenko Zool. Zh. 59: 225 (1980).

Gland extract vs. volatile collection (example No. 1)

In *A. sordidus*, in gland extracts large amounts of (*E,E*)-farnesyl hexanoate were present, with only traces in volatile collections.

glands



volatiles

ratio
ger:farn = 1:<0.1

?

This chromatogram shows the composition of volatile collections. The x-axis represents time in minutes, with major ticks at 15, 20, 25, 30, 35, 40, 45, and 50. A very large peak is visible at approximately 26 minutes, labeled 'geranyl hexanoate'. A very small peak is visible at approximately 50 minutes, labeled with a question mark '?'. The text 'ratio ger:farn = 1:<0.1' indicates that the amount of *E,E*-farnesyl hexanoate is significantly lower than that of geranyl hexanoate.



A. sordidus

Photo J. Vuts

Gland extract vs. volatile collection (example No. 1)

In field tests on *A. sordidus*, no influence of the addition of the farnesyl compound could be observed.

glands

ratio
ger:farn = 1:1

int. std.

E,E-farnesyl
hexanoate

geranyl
hexanoate

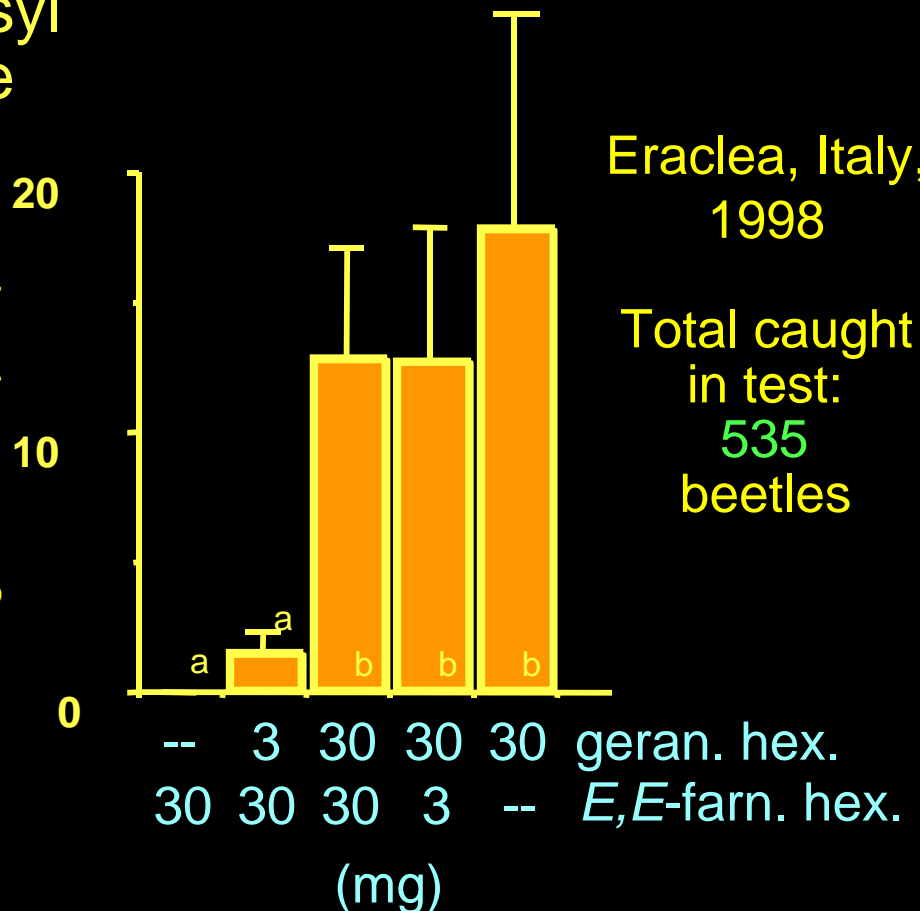
volatiles

ratio
ger:farn = 1:<0.1

?

15 20 25 30 35 40 45 50 50 min

average catch/trap/inspection



Eraclea, Italy,
1998

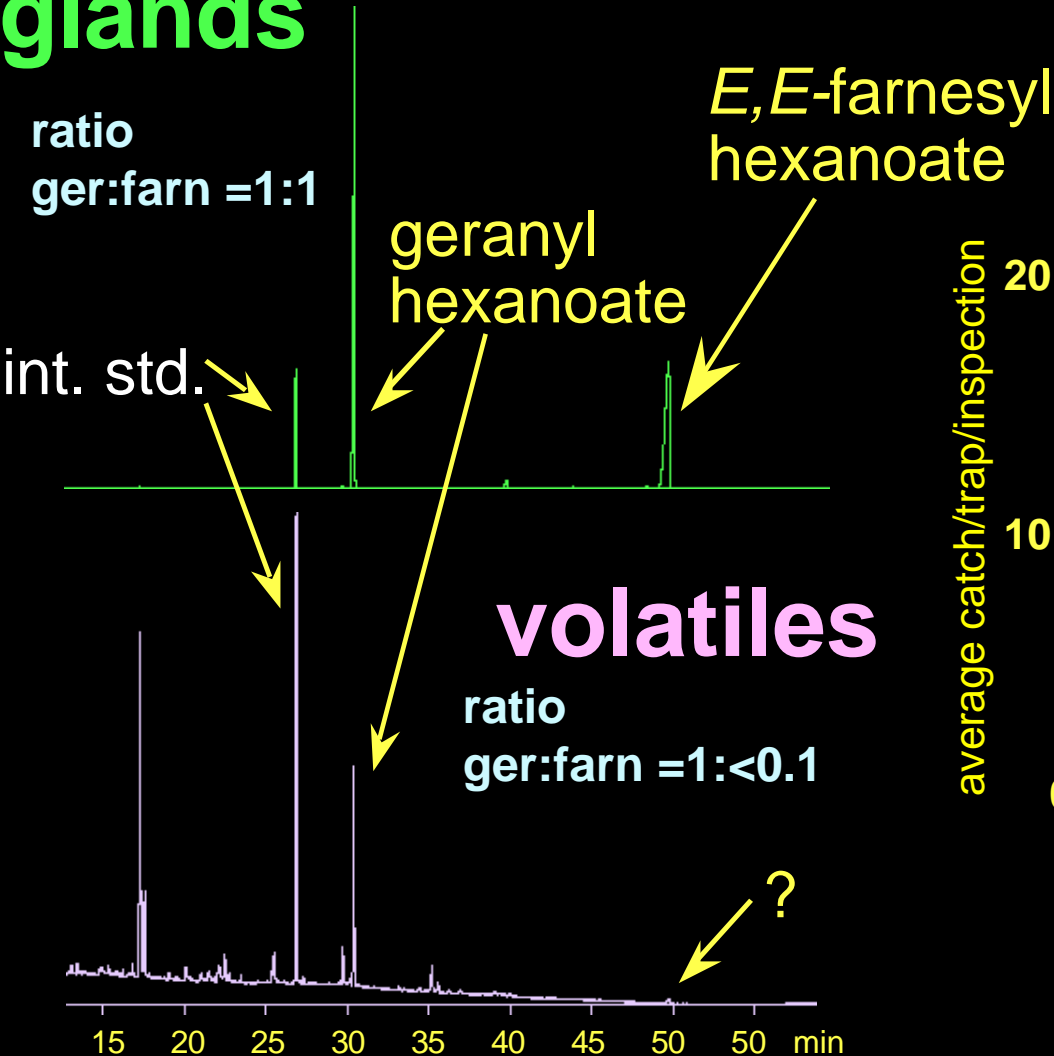
Total caught
in test:
535
beetles

(after Tóth M, et al., unpublished)

Gland extract vs. volatile collection (example No. 1)

Consequently, by definition, only geranyl hexanoate can be termed a pheromone component in this species.

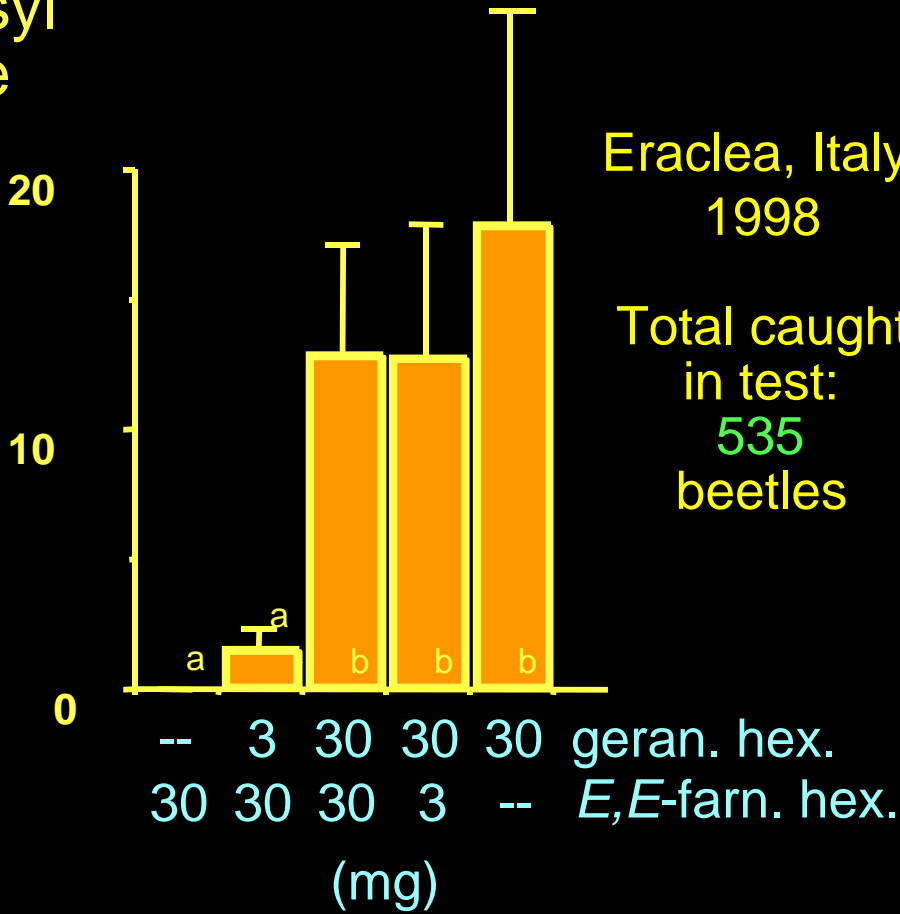
glands



volatiles

ratio
ger:farn = 1:<0.1

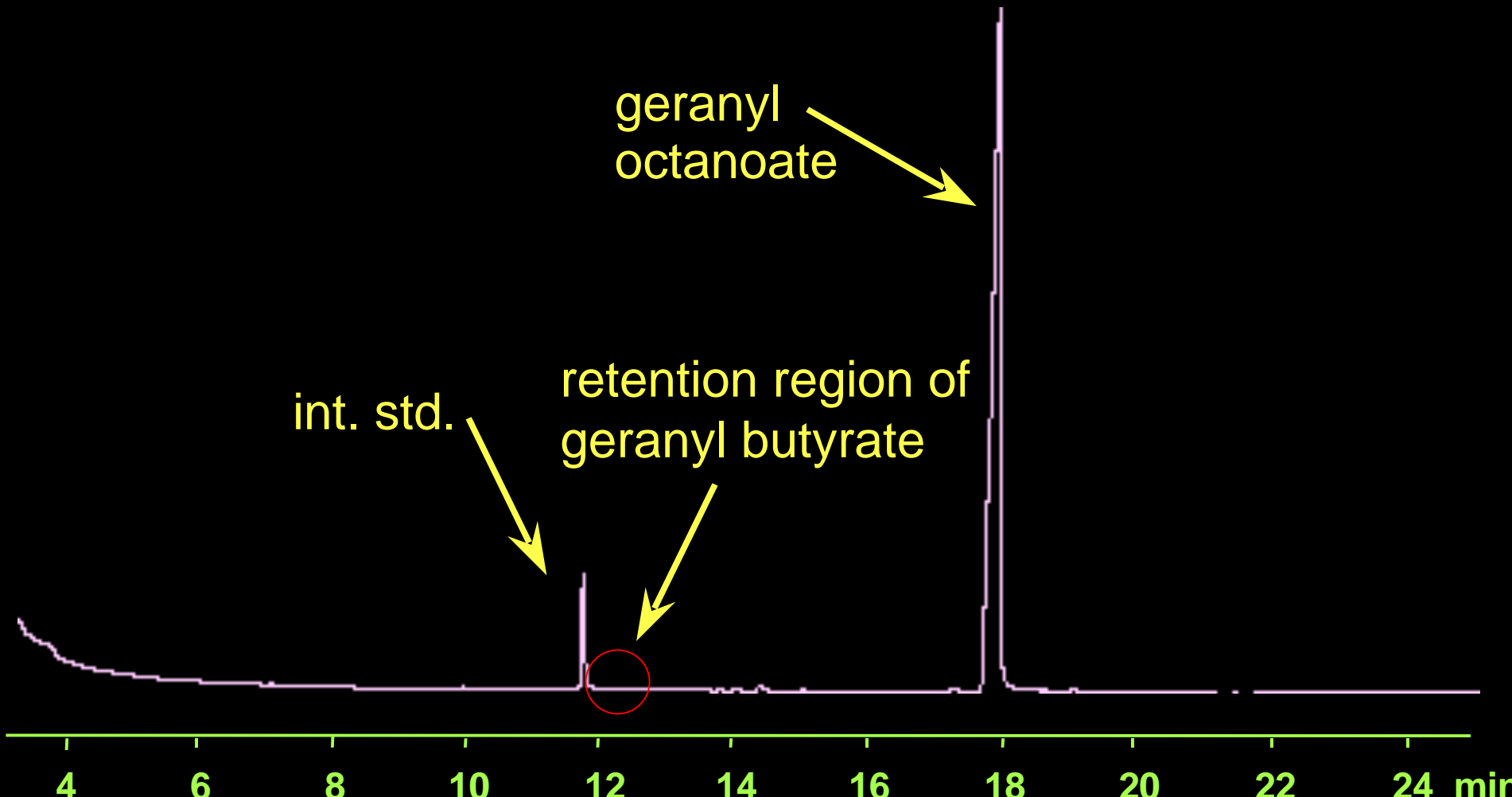
average catch/trap/inspection



(after Tóth M, et al., unpublished)

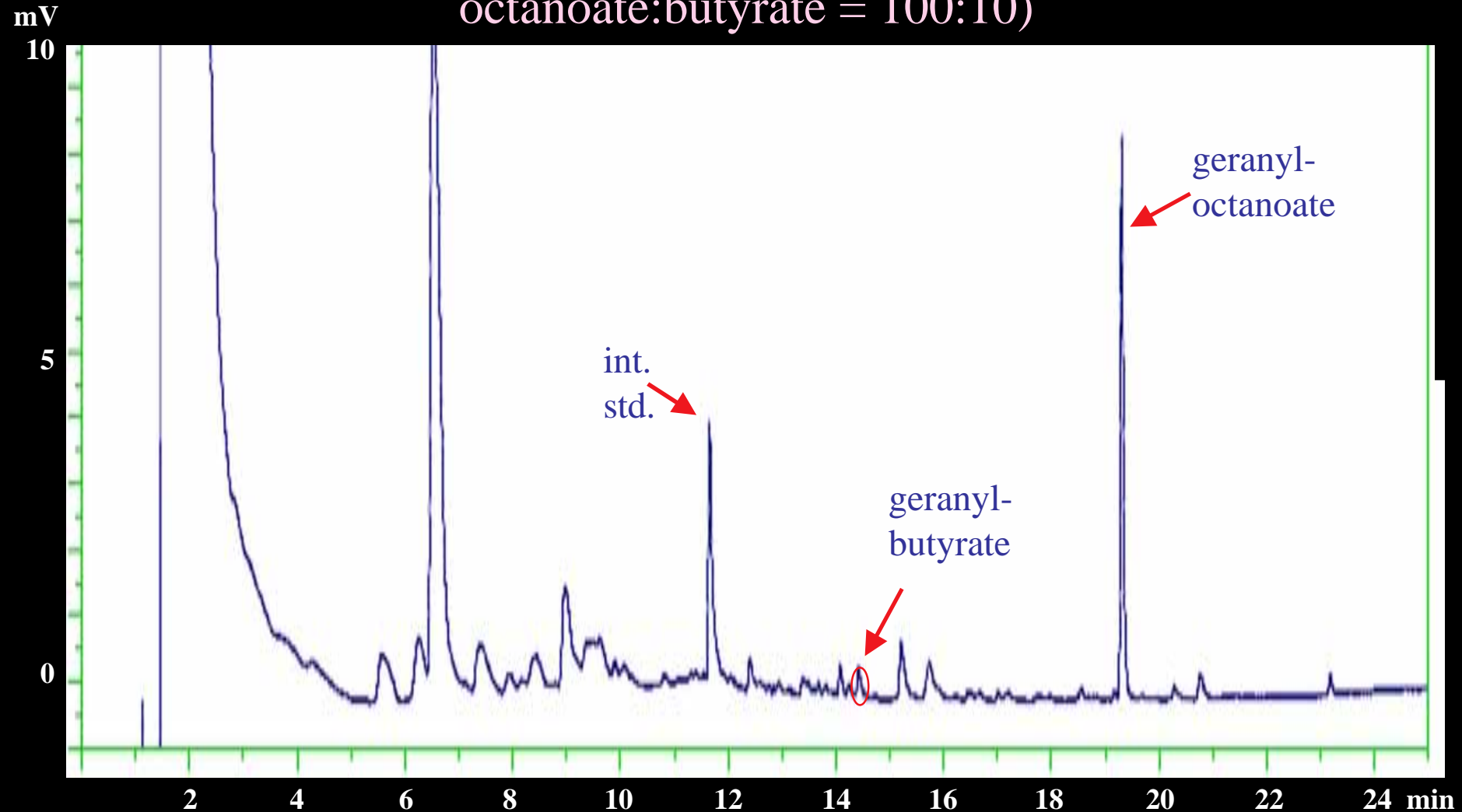
Gland extract vs. volatile collection (example No. 2)

Gland extracts of *A. lineatus* were dominated by a single very large peak of geranyl octanoate, geranyl butyrate was hardly detectable (ratio of octanoate:butyrate = 100:<0.01)



Gland extract vs. volatile collection (example No. 2)

In volatile collections the butyrate was well visible (ratio of octanoate:butyrate = 100:10)




(After Vuts J. et al., in preparation)

Gland extract vs. volatile collection (example No. 2)

In the field the presence of the butyrate was absolutely necessary for attraction.

Total caught
in test:
279
beetles

Rümlang,
May 23 -
August 14,
1997




	Geranyl octanoate	Geranyl butanoate	E,E-farnesyl acetate	Geraniol	Geranyl hexanoate	Neryl isovalerate	<i>A.lineatus</i>
	10	0
	30	2
	100	0
	10	1	273
	10	.	1	.	.	.	2
	10	.	.	1	.	.	1
	10	.	.	.	1	.	0
	10	1	1

Gland extract vs. volatile collection (example No. 2)

It appears that volatile collections reflect better the true pheromone composition of a given species than gland extracts do.

Total caught
in test:
279
beetles

Rümlang,
May 23 -
August 14,
1997



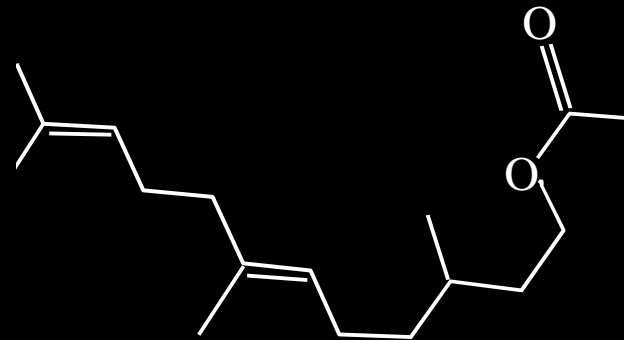
	Geranyl octanoate	Geranyl butanoate	E,E-farnesyl acetate	Geraniol	Geranyl hexanoate	Neryl isovalerate	<i>A. lineatus</i>
	10	0
	30	0
	100	0
	10	1	273
	10	.	1	.	.	.	2
	10	.	.	1	.	.	1
	10	.	.	.	1	.	0
	10	1	1

Geometrical isomers

Another reason for inactivity of identified structures may be that in some cases geometrical purity of synthetic compounds is crucial - as commonly found also in moth pheromones.

It is well known that *Agriotes ustulatus* responds only to synthetic (*E,E*)-farnesyl acetate batches which have >95% (*E,E*) geometric purity.

Presence of higher percentages of the other isomers inhibits catches.



(*E,E*)-farnesyl acetate



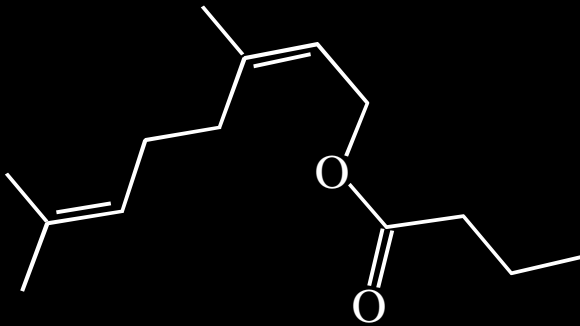
Agriotes ustulatus

www.elateridae.com

Geometrical isomers

A recent report described the first neryl ester (nerol is the geometrical isomer of geraniol) as a pheromone component in *Agriotes acuminatus* also suggesting the importance of geometrical isomerism in click beetles.

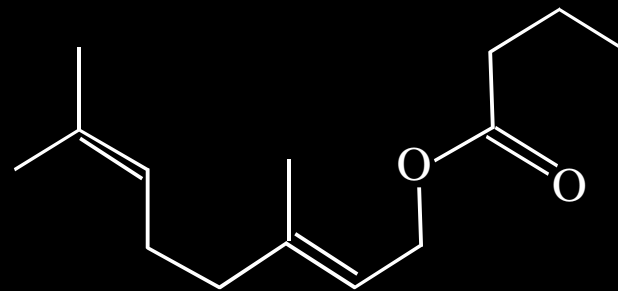
“Good” isomer



neryl butyrate

[(Z)-3,7)-dimethyl-2,6-
octadienyl butyrate]

“Wrong” isomer



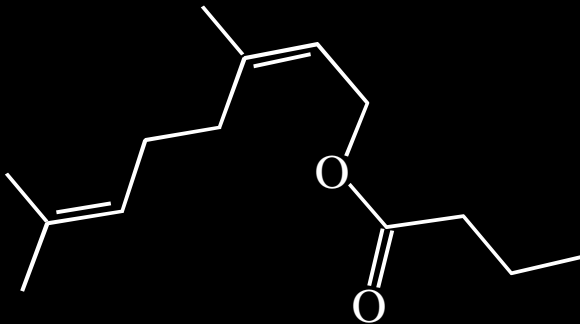
geranyl butyrate

[(E)-3,7)-dimethyl-2,6-
octadienyl butyrate]

Geometrical isomers

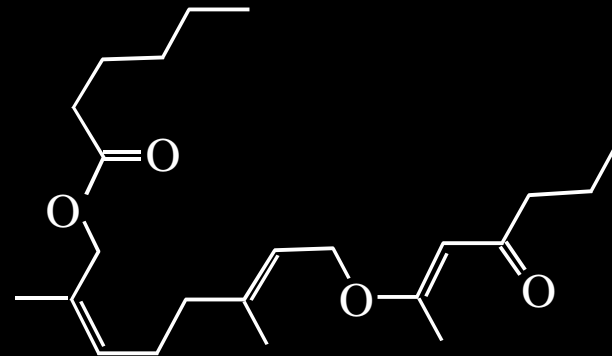
The full pheromone composition in *A. acuminatus* contained also another ester with an unusual structure, which was necessary for field activity.

“Good” isomer



neryl butyrate
[(*Z*)-3,7)-dimethyl-2,6-
octadienyl butyrate]

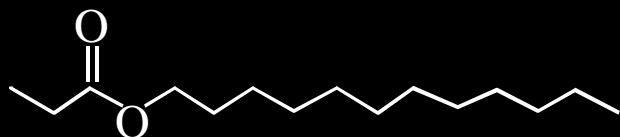
second component



(*Z,E*)-2,6-dimethyl-
2,6-octadien-1,8-diyl
dihexanoate]

Other structures

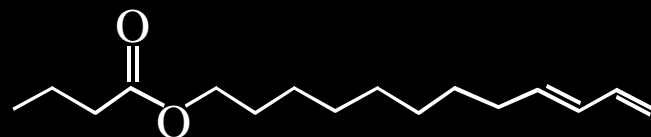
Some *Melanotus* spp. from the far east appear to use dodecenyl compounds (structurally similar to moth pheromones)



dodecyl acetate

Melanotus okinawensis

Tamaki Jpn KokaiTokyo Koho
JP 61:12601 (1986)



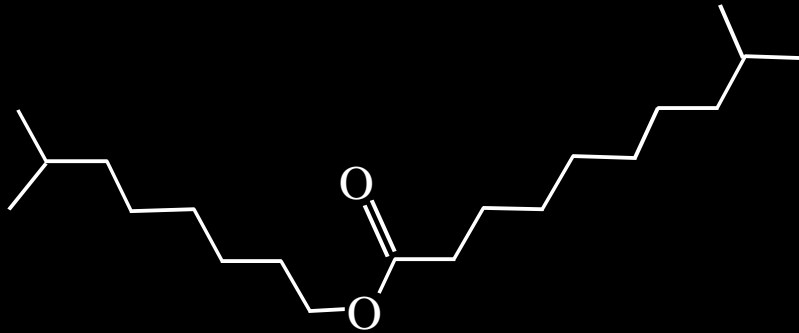
(*E*)-9,11-dodecadienyl acetate

Melanotus sakishimensis,
M. tamsuyensis

Iwanaga, Appl. Ent. Zool. 35:283 (2000)
Yen, Syn. Comm. 28:4561 (1998)

Other structures

As new structure, a methyloctanol ester has been identified from the non-pest *Ectinus aterrimus* click beetle.



7-methyloctyl 9-
methyldecanoate

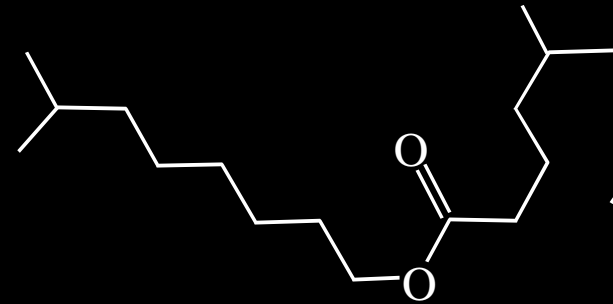
Ectinus aterrimus

Tolasch Chemoecology 18:177 (2008)

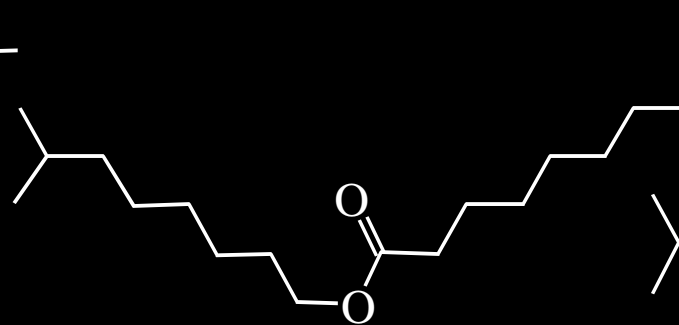


Other structures

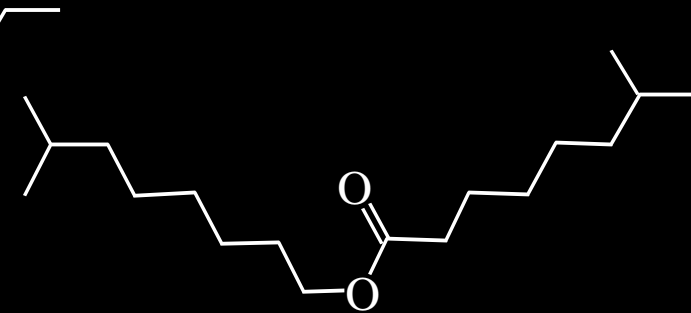
Four similar esters were recently shown out from *E. ferrugineus*, an endangered click beetle.



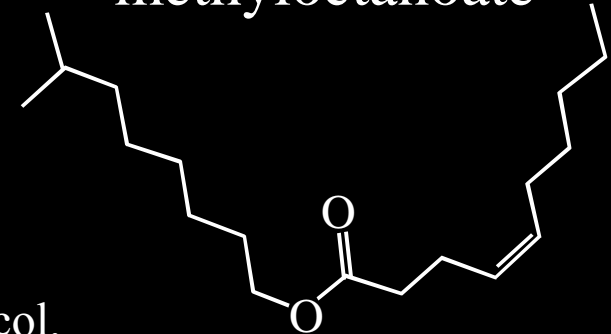
7-methyloctyl 5-methylhexanoate



7-methyloctyl octanoate



7-methyloctyl 7-methyloctanoate



7-methyloctyl (Z)-4-decenoate

Elater ferrugineus

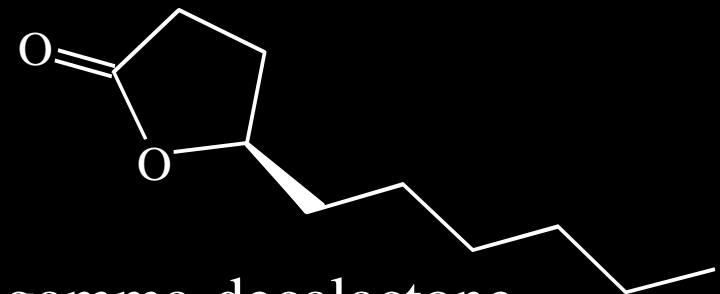
www.nhmus.hu

Tolasch J. Chem. Ecol.
33:2156 (2007)

Other structures

Kairomonal effect:

E. ferrugineus also is attracted to the pheromone of its prey, *Osmoderma eremita* (Scarabaeidae).

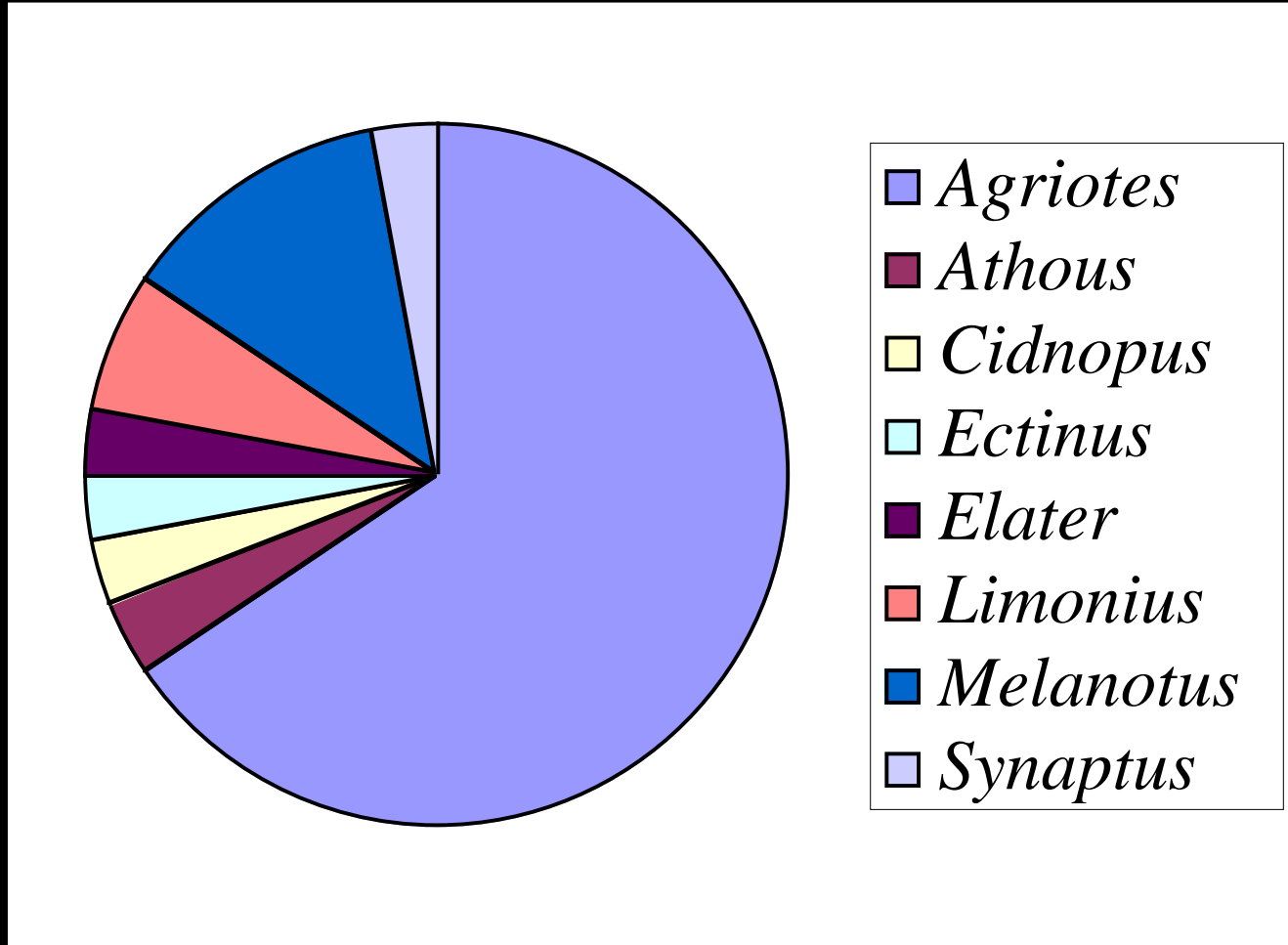


(*R*)-gamma-decalactone

Svensson J. Chem. Ecol. 30:353 (2004)

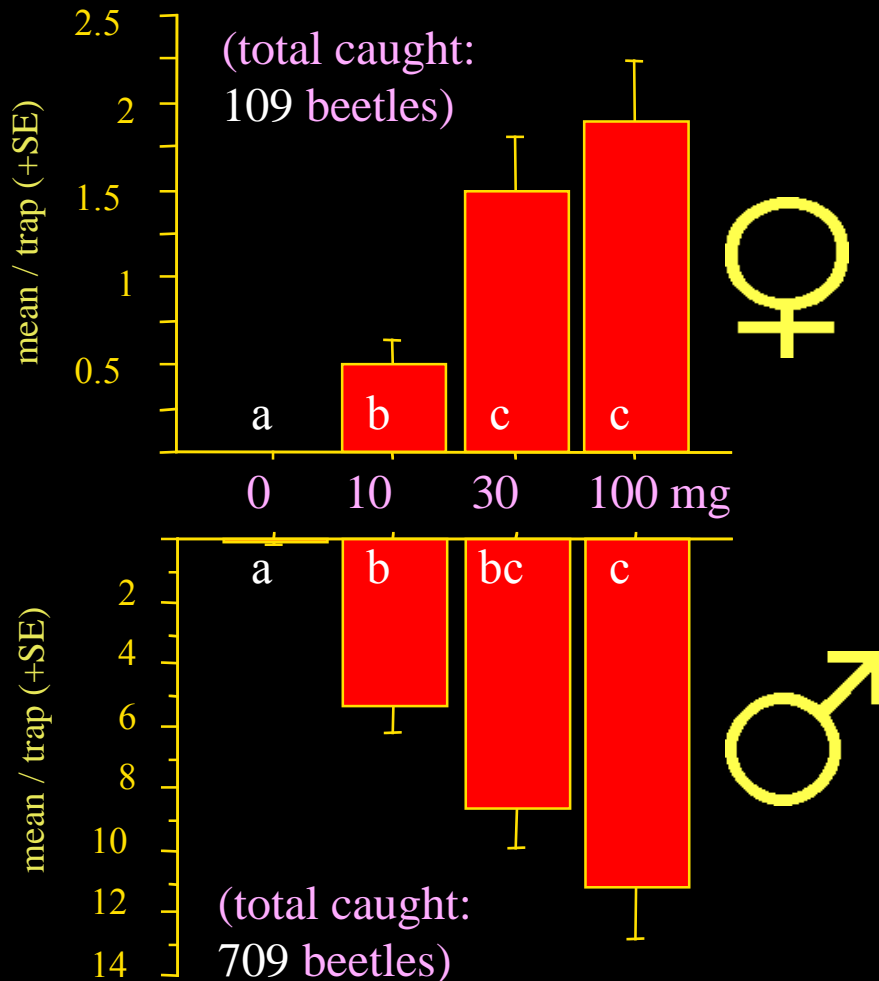
Pheromone information in click beetle genera

At present we have some information on chemical structures in 34 spp.
Information on the genus *Agriotes* predominates.



Females responding to the pheromone

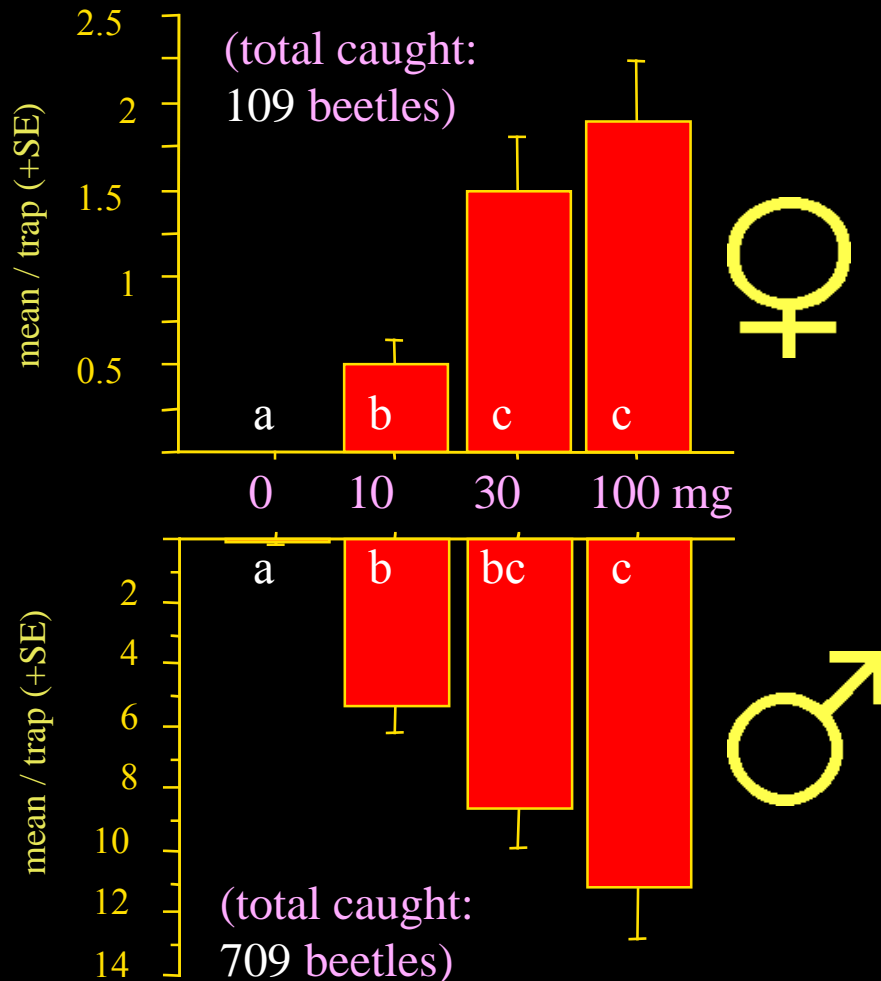
Traditionally it was thought that in click beetles only males respond to the pheromone (as in the case of “classical” sex pheromones).



Catches of male and female *A. sordidus* in traps baited with different doses of the pheromone (Italy, Veneto, May 1 - 26, 2001, Furlan et al., unpubl.)

Females responding to the pheromone

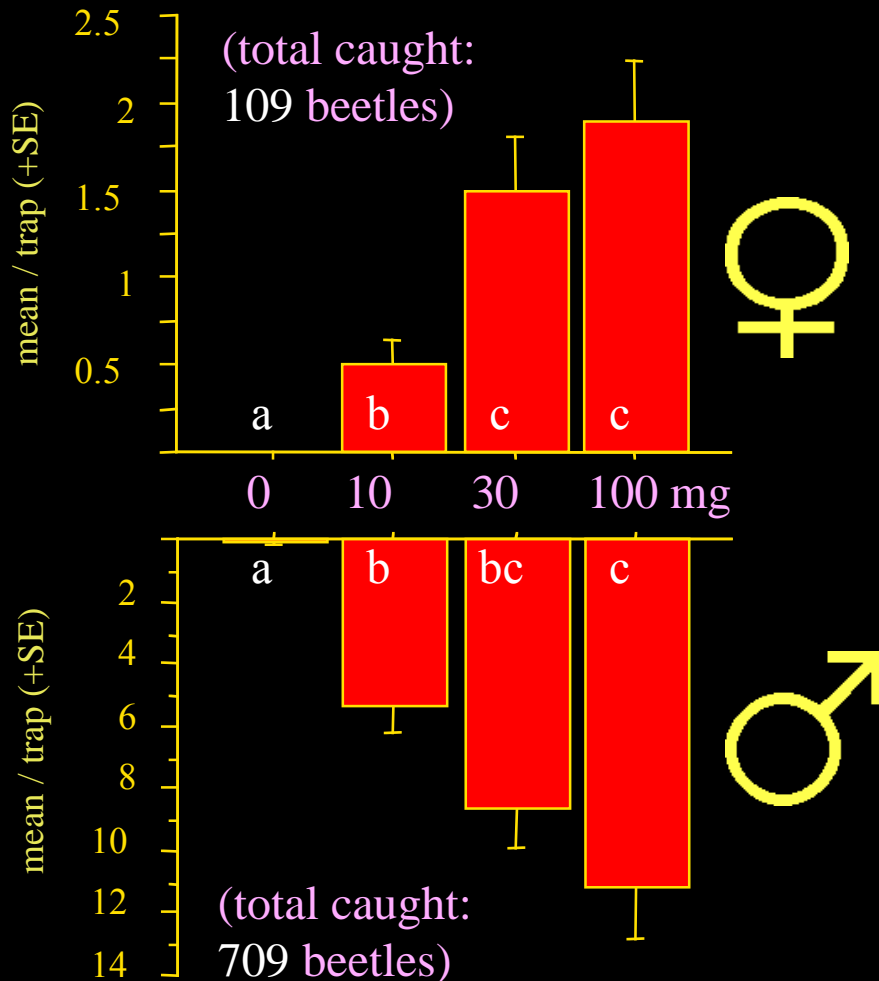
However, L. Furlan observed that in traps of *A. sordidus* baited with synthetic pheromone, sizeable catches of females (besides large catches of males) were recorded



Catches of male and female *A. sordidus* in traps baited with different doses of the pheromone (Italy, Veneto, May 1 - 26, 2001, Furlan et al., unpubl.)

Females responding to the pheromone

Female catches also showed a dose response, suggesting that the pheromone showed true attraction in female *A. sordidus*.



Catches of male and female *A. sordidus* in traps baited with different doses of the pheromone (Italy, Veneto, May 1 - 26, 2001, Furlan et al., unpubl.)

Females responding to the pheromone

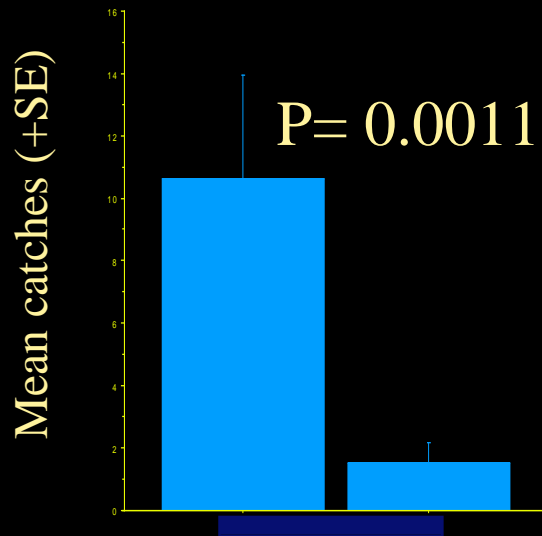
Attraction of females to the respective synthetic pheromone has been confirmed in several species, so the case of *A. sordidus* is not unique.

A. brevis

pheromone components:
(*E,E*)-farnesyl butyrate +
geranyl butyrate

Eraclea, Italy, 2000

Total caught: 194 beetles



pheromone
bait

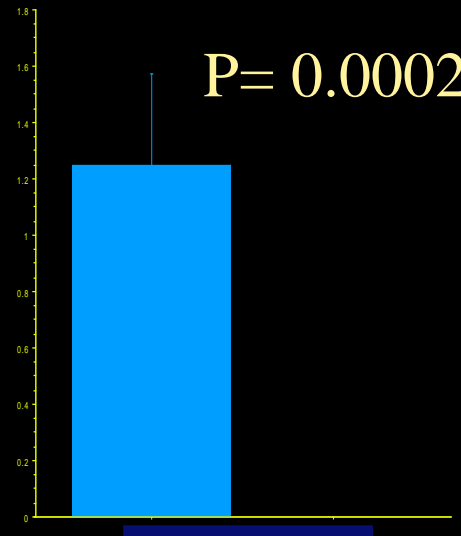


A. ustulatus

pheromone component:
(*E,E*)-farnesyl acetate

Eraclea, Italy, 2000

Total caught: 20 beetles

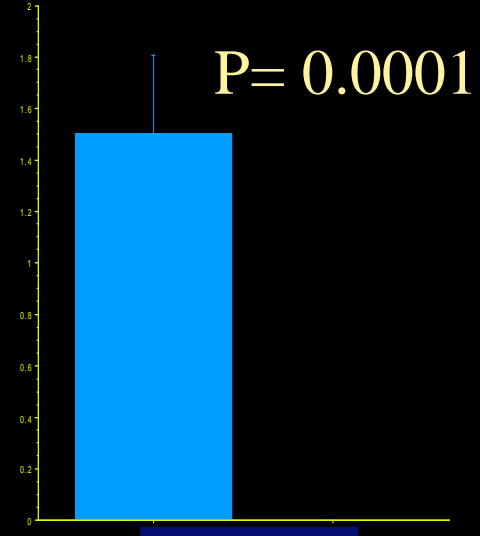


A. sordidus

pheromone component:
geranyl hexanoate

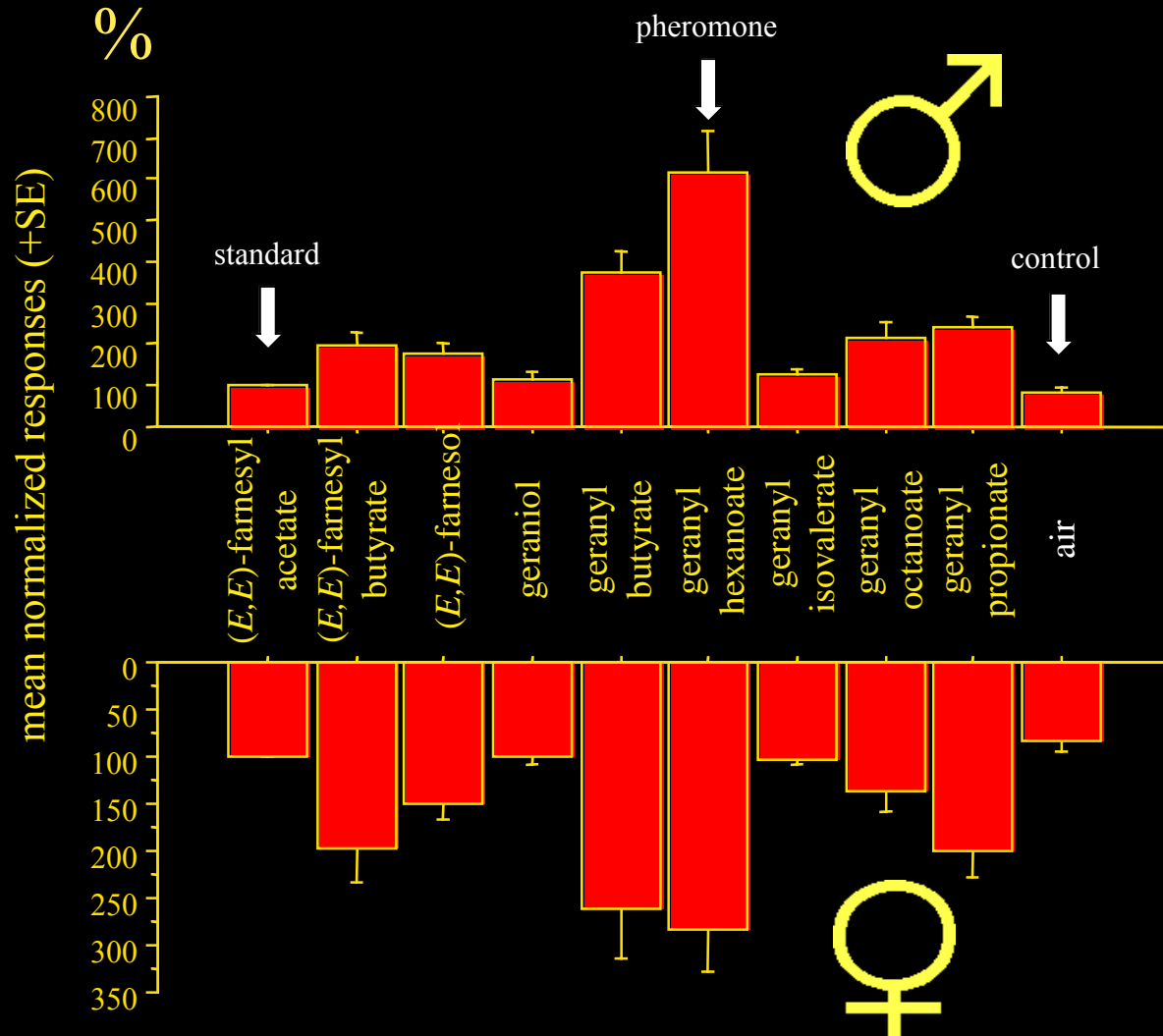
Berton-Greggio, Italy, 2001

Total caught: 42 beetles



Females responding to the pheromone

What is more, female antennae responded well to the pheromone and gave similar response spectra in EAG to that of male antennae.



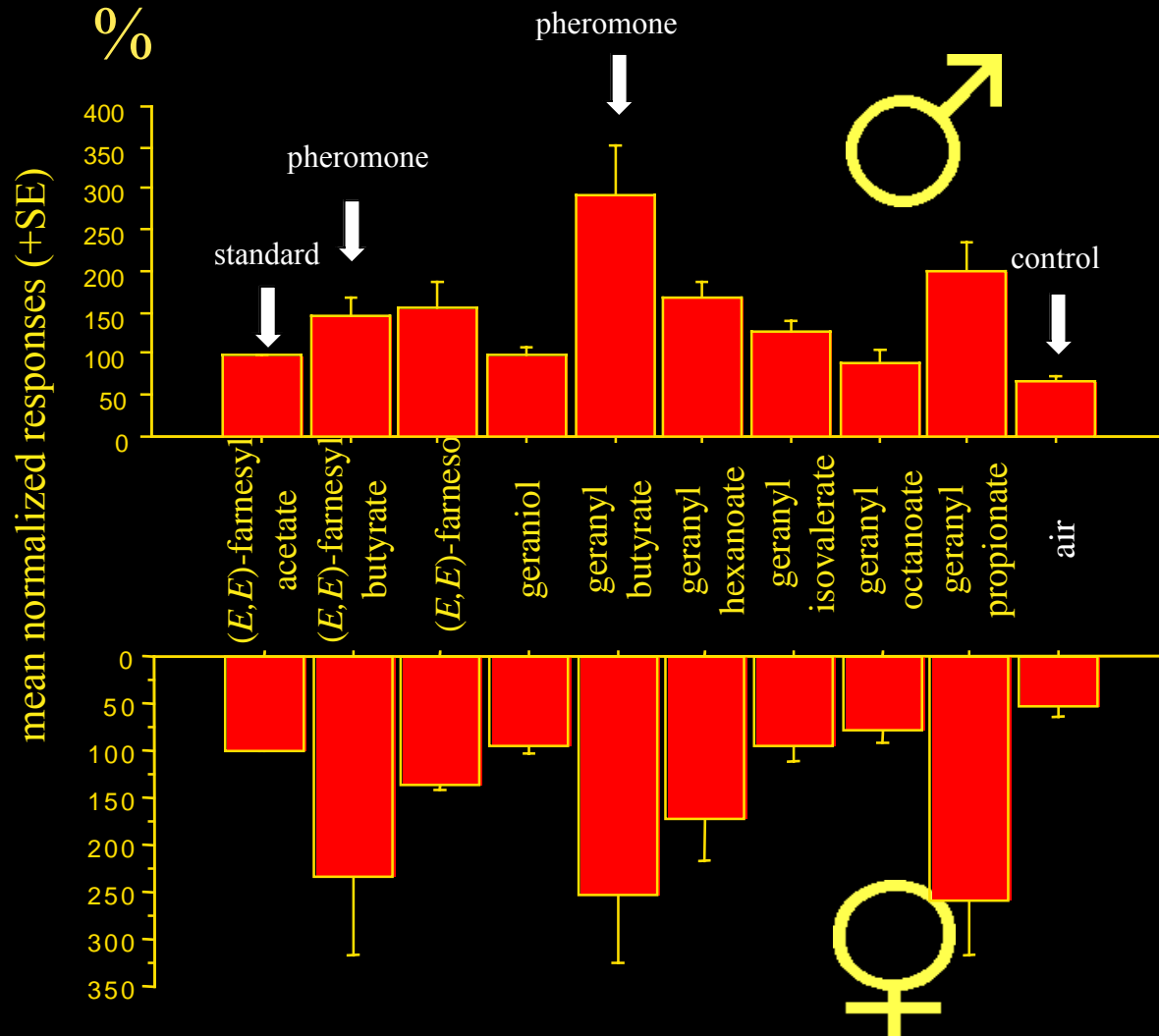
(after Vuts J. et al., unpublished)

Agriotes sordidus

Females responding to the pheromone

This again was true to a number of species, and strongly suggested that females are capable to perceive their respective pheromone components.

Agriotes brevis

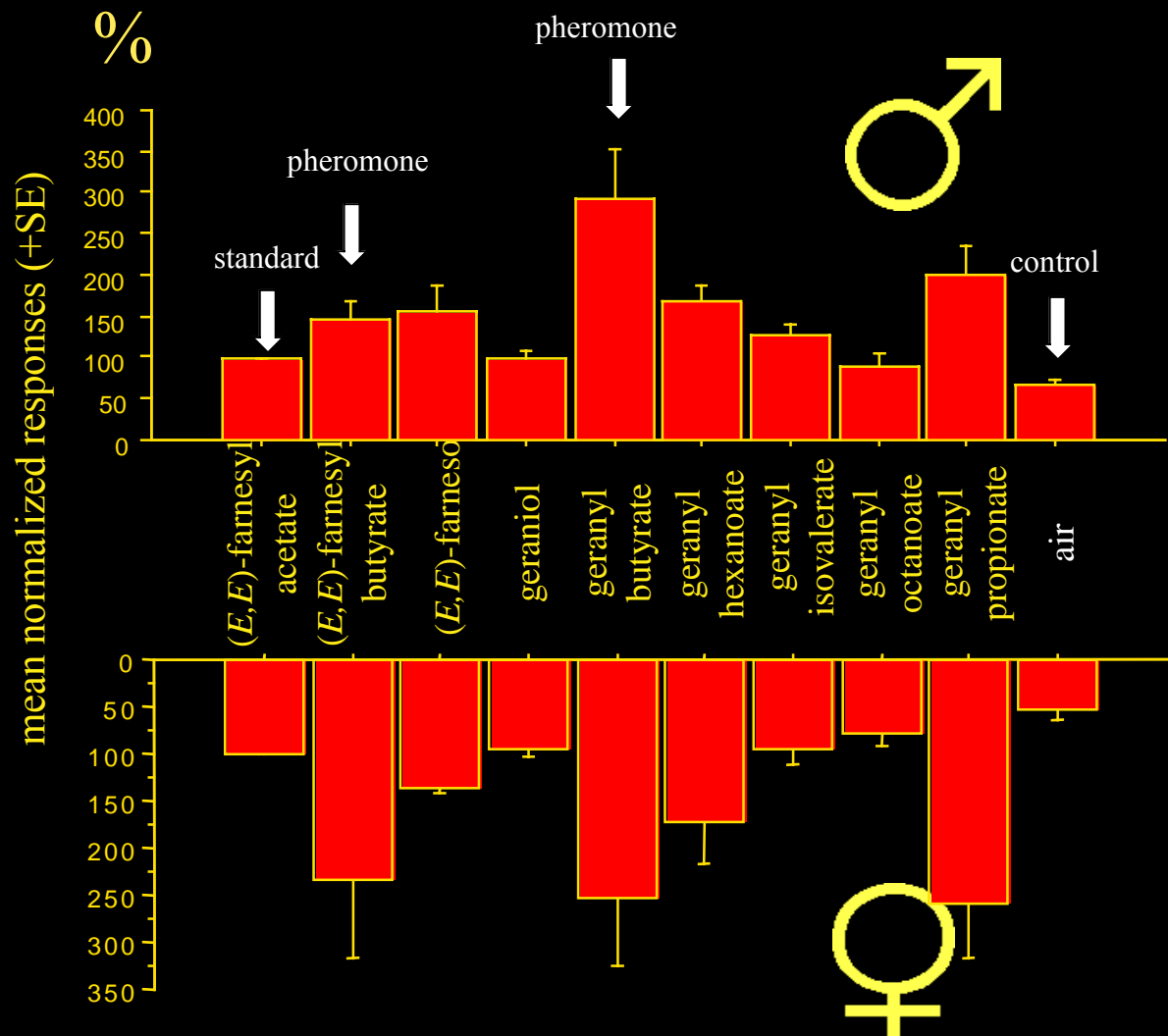


(after Vuts J. et al., unpublished)

Females responding to the pheromone

This brings up the possibility that the pheromones of click beetles are wrongly classified into the “classical” sex pheromone category.

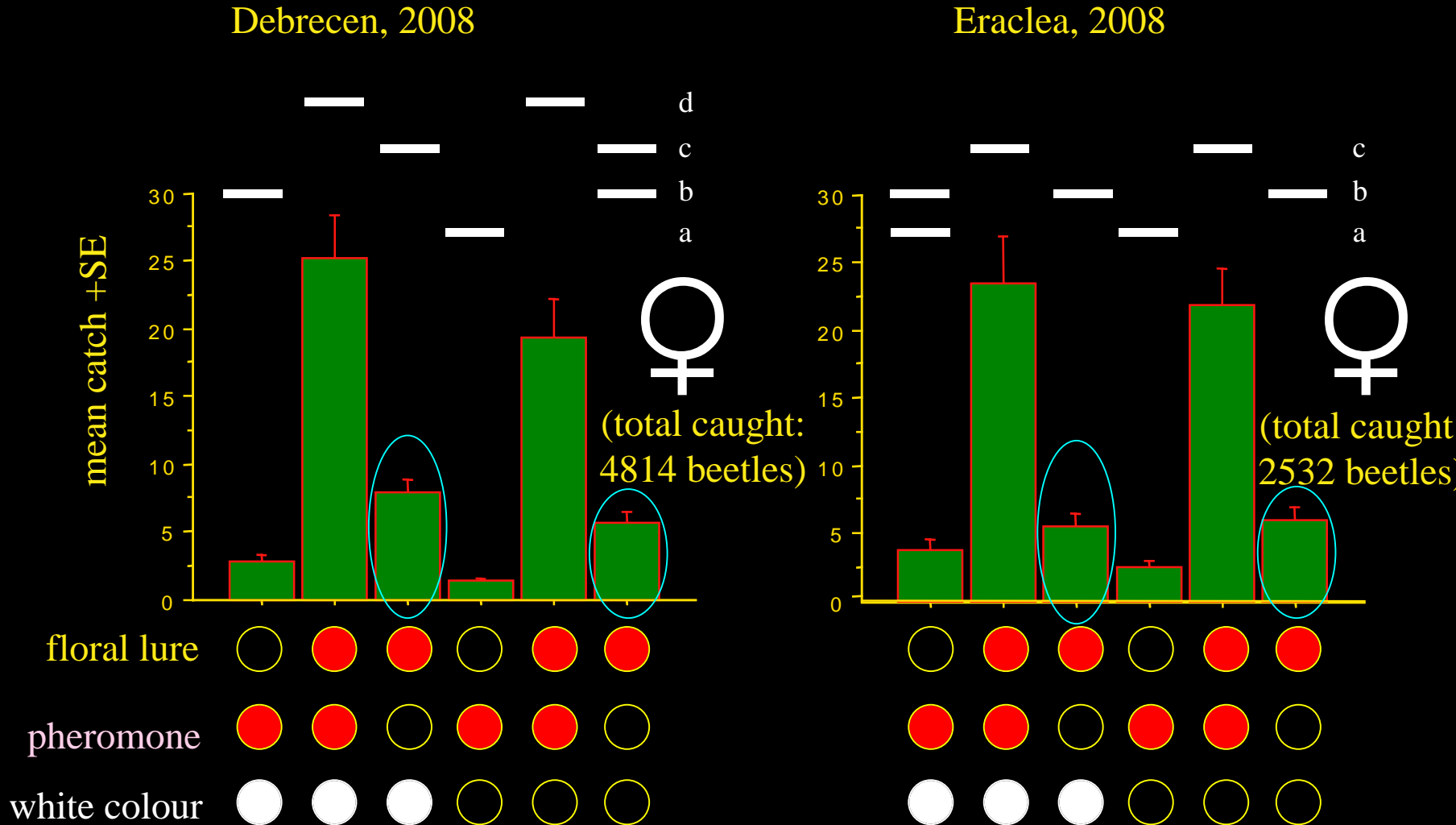
Agriotes brevis



(after Vuts J. et al., unpublished)

Sex pheromone vs. aggregation pheromone?

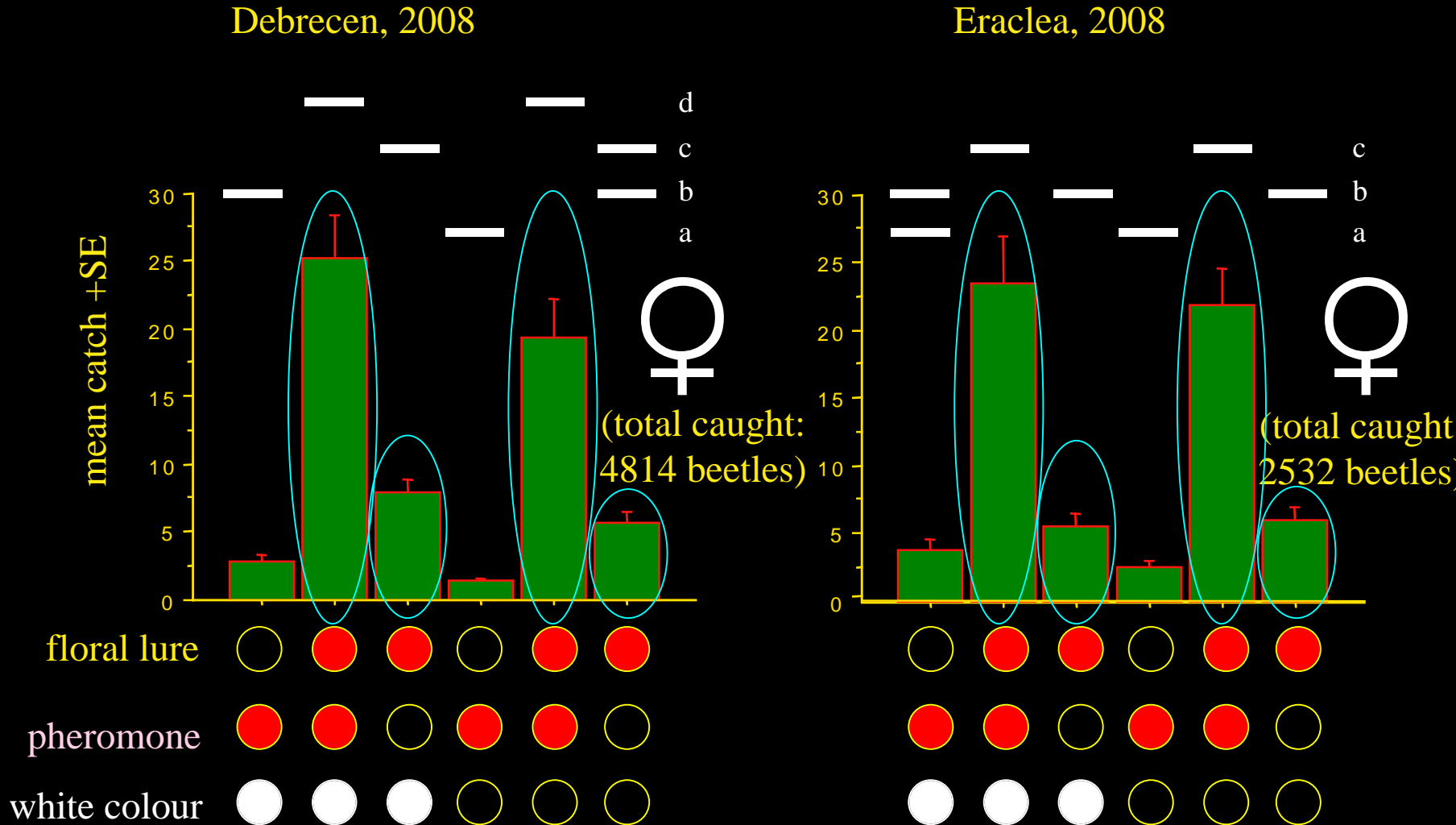
In *A. ustulatus*, a floral lure has been discovered, which attracts females.
 (White colour as attractive visual cue showed negligible influence)



(After Tóth M. et al., in preparation)

Sex pheromone vs. aggregation pheromone?

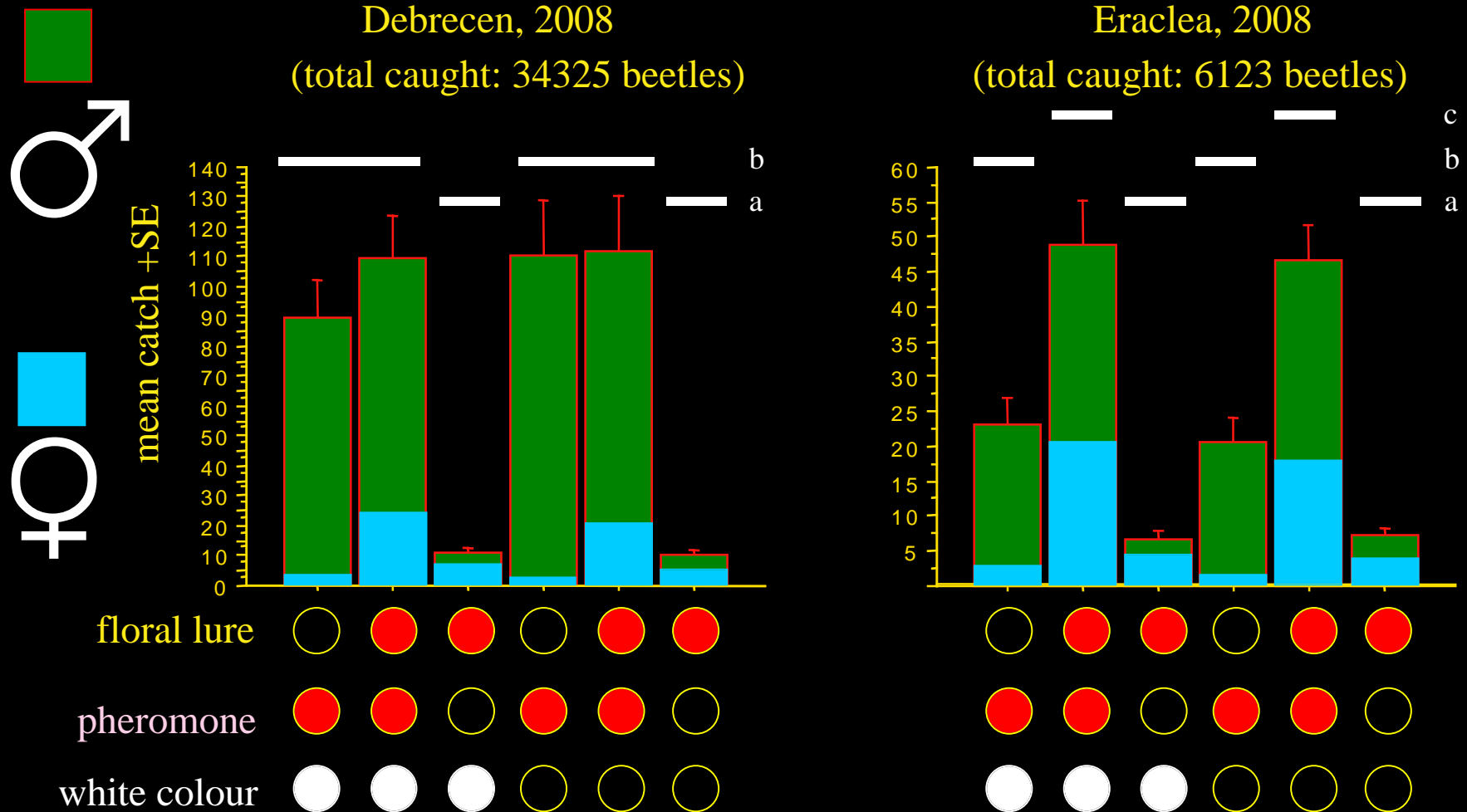
The addition of the pheromone to the floral lure in the same trap increases catches of females!



(After Tóth M. et al., in preparation)

Sex pheromone vs. aggregation pheromone?

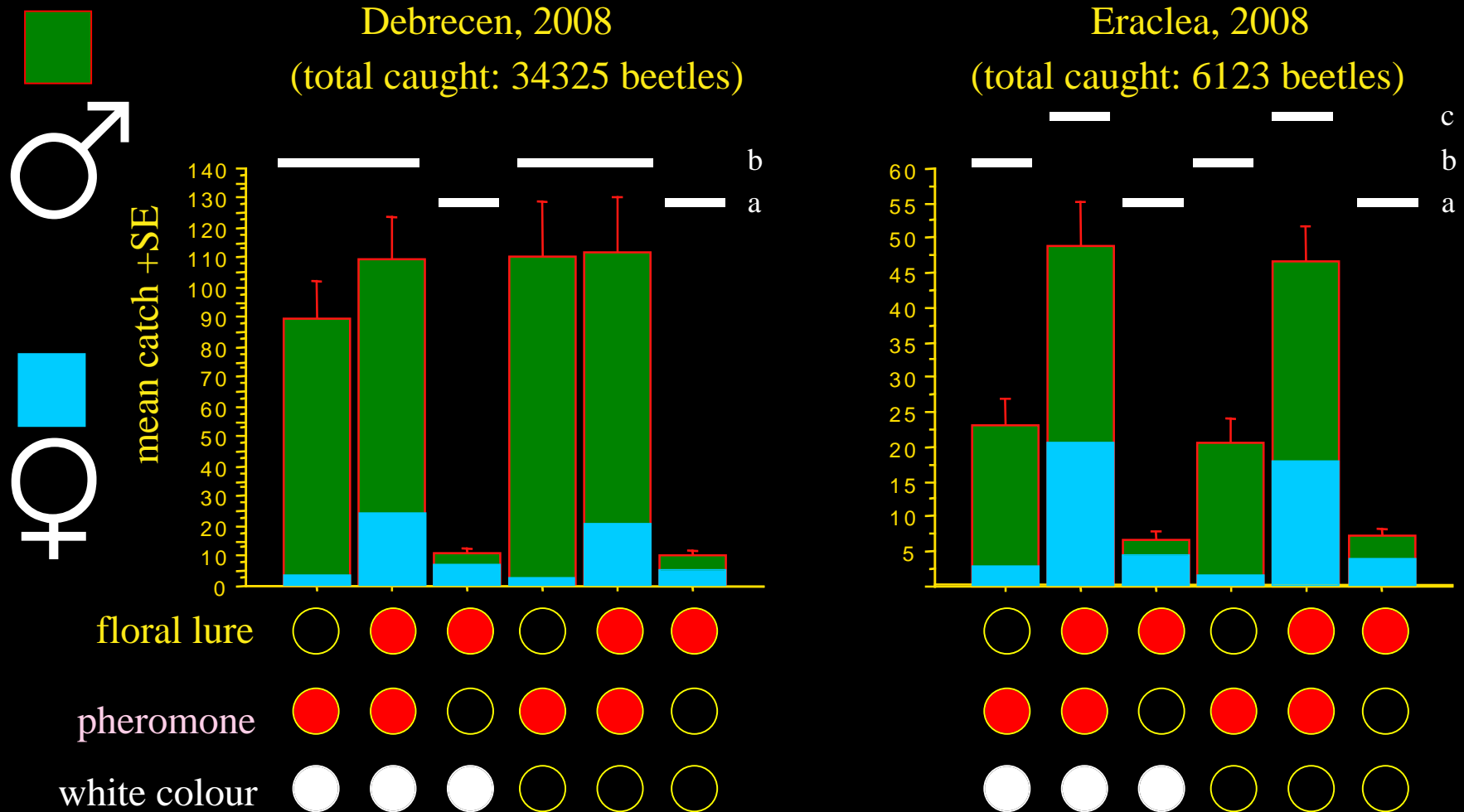
Most female specimens are caught in traps with both floral AND pheromonal baits



(After Tóth M. et al., in preparation)

Sex pheromone vs. aggregation pheromone?

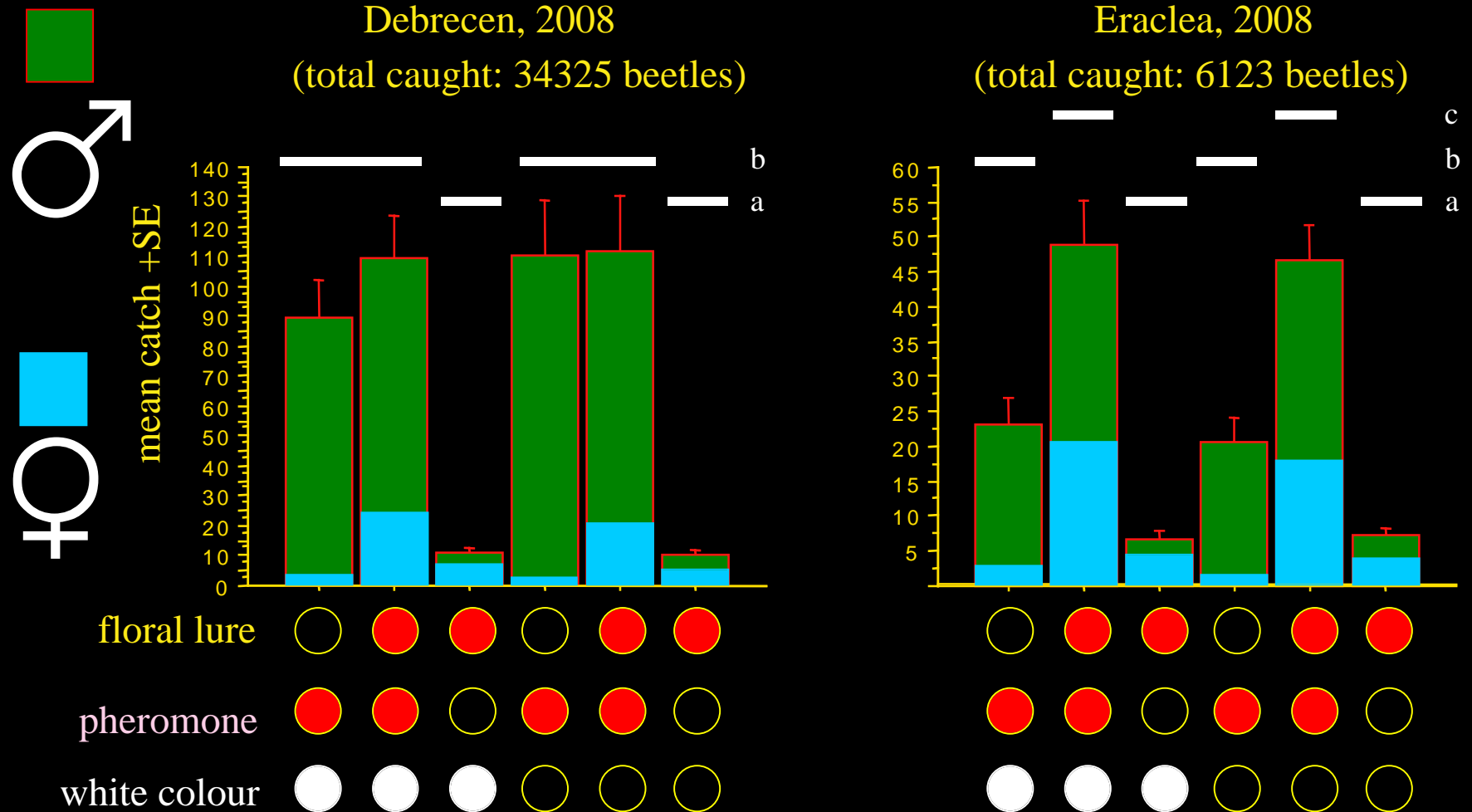
A similar phenomenon (that the presence of the pheromone increases the effect of floral bait on females) is unusual with sex pheromones



(After Tóth M. et al., in preparation)

Sex pheromone vs. aggregation pheromone?

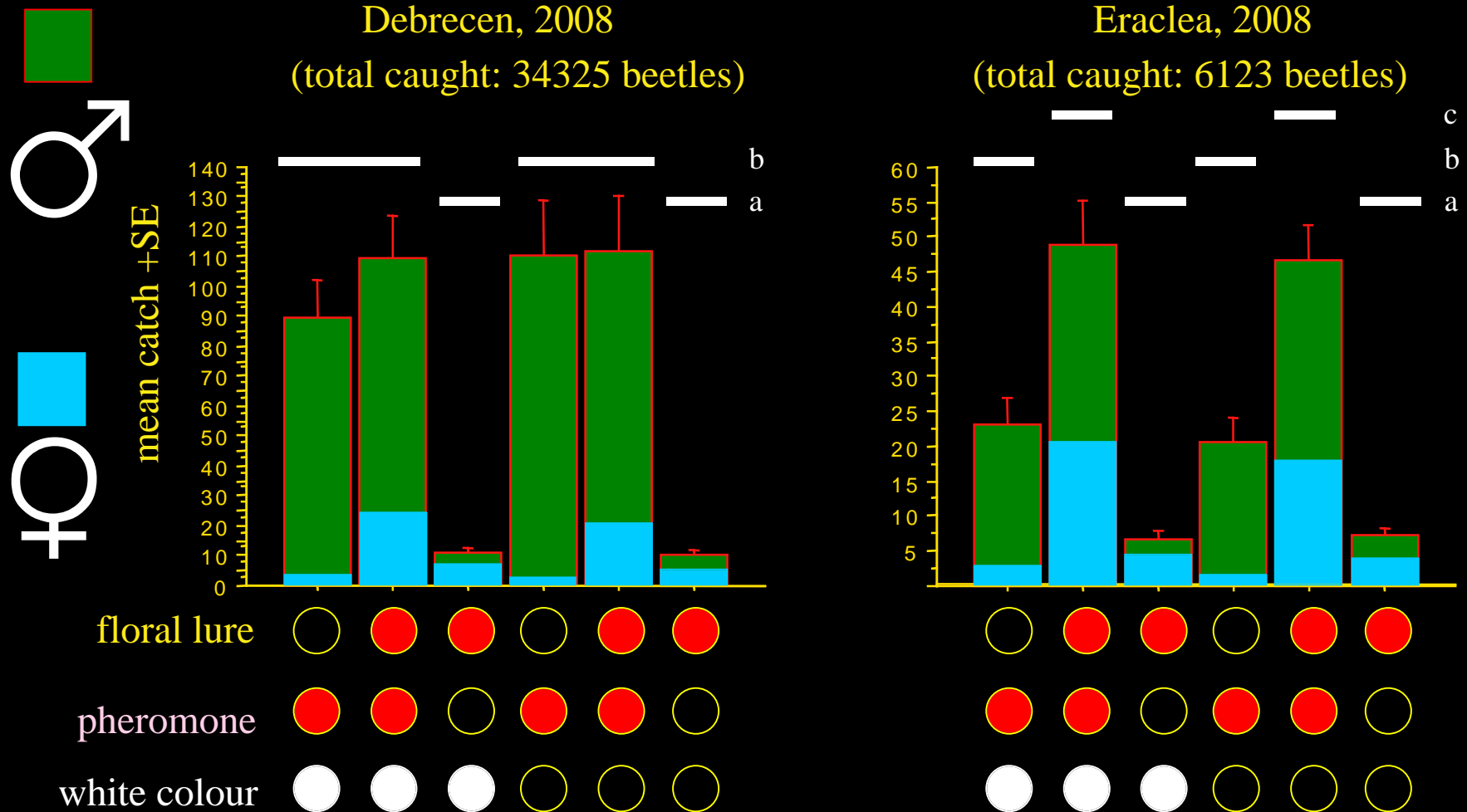
However, it is frequently reported with aggregation pheromones



(After Tóth M. et al., in preparation)

Sex pheromone vs. aggregation pheromone?

This again suggests that the pheromone of *Agriotes* click beetles is not a “classical” sex pheromone



(After Tóth M. et al., in preparation)

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unpublished results shown:

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Tolasch, T. (Germany)

Toshova, T. (Bulgaria)

Vuts, J. (Hungary)

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