Family Message to the American Chemical Society on behalf of Dr. Agnes Rimando

On behalf of our family, allow me to express our sincerest thanks to the ACS for holding two symposia in honor of my sister Agnes Rimando who passed away a year ago. Probably there is no better way to honor her memory and we are deeply grateful. This gesture reminds us how she is very much appreciated by this great professional society of scientists and dedicated researchers. Your honoring her today certainly helps in alleviating the grief we still feel following her passing. Jane's notification of these sessions in honor of Agnes came down to us like the proverbial oasis in a parched desert of grief, for the memory of our beloved Agnes is kept alive once more even if only for two days. Our family will always remember your kindness. Thank you Jane, especially for delivering this message for us. And thanks as well to Dr. Stephen Duke, mentor and adviser to Agnes, for all his help during the most difficult times we went through last year when Agnes fell ill and passed away. His advice and assistance on matters we needed to attend to consequent to Agnes's demise helped immeasurably in lessening our anxiety in facing them.

Our family considers Agnes the "scientist" of the clan. Perhaps the earliest indications of her scientific inclination were her winning science fair prizes at our local high school. Looking back now, we believe those were the seeds that would blossom later into a highly productive and meaningful career in her chosen field. Agnes earned her B. S. Pharmacy at the University of the Philippines, the state university which trains its students with research discipline and imbues them with pursuit of excellence. That's where Agnes would develop her deep interest in research and hone her rigorous laboratory skills. She became an instructor for a few years at the University of the Philippines, but her adventurous streak and the desire to further upgrade her capabilities earned her short stints outside the Philippines, as a research associate in South Korea and Japan. These exposures would culminate in a Master's degree in 1985. Not content with being a small fish in a small pond, Agnes sought greater challenges, moving to Chicago to earn her Doctorate in Pharmacognosy from Univ. of Illinois (UIC).

Our family hoped that Agnes would return to the Philippines. But she opted to stay in the U.S. "for a little while" and took on a job with the USDA which she would serve with dedication until her passing away last year. What was supposed to be a temporary stay became longer until she took on permanent residency and eventually became a citizen. Agnes explained that her work in USDA gave her opportunities requisite to professional advancement. If that's where she would find fulfillment, our family understood and gave its full support.

And so it was that Agnes would blaze a trail of scientific research and contributions. We would hear of her work, publications, delivering papers here and there, and her travels to other countries representing the U.S. government. Probably what would rank as her highest achievement would be the discovery of the compound "pterostilbene" in blue berries. The compound has proven to be of tremendous medicinal value. As an engineer, I know what this meant for her. I kidded her at one point about her "discovery" that I found hard to pronounce much less spell correctly. This discovery became synonymous with if not inextricably linked to her. Agnes also became a prolific scientific writer, authoring or co-authoring more than 200 papers.

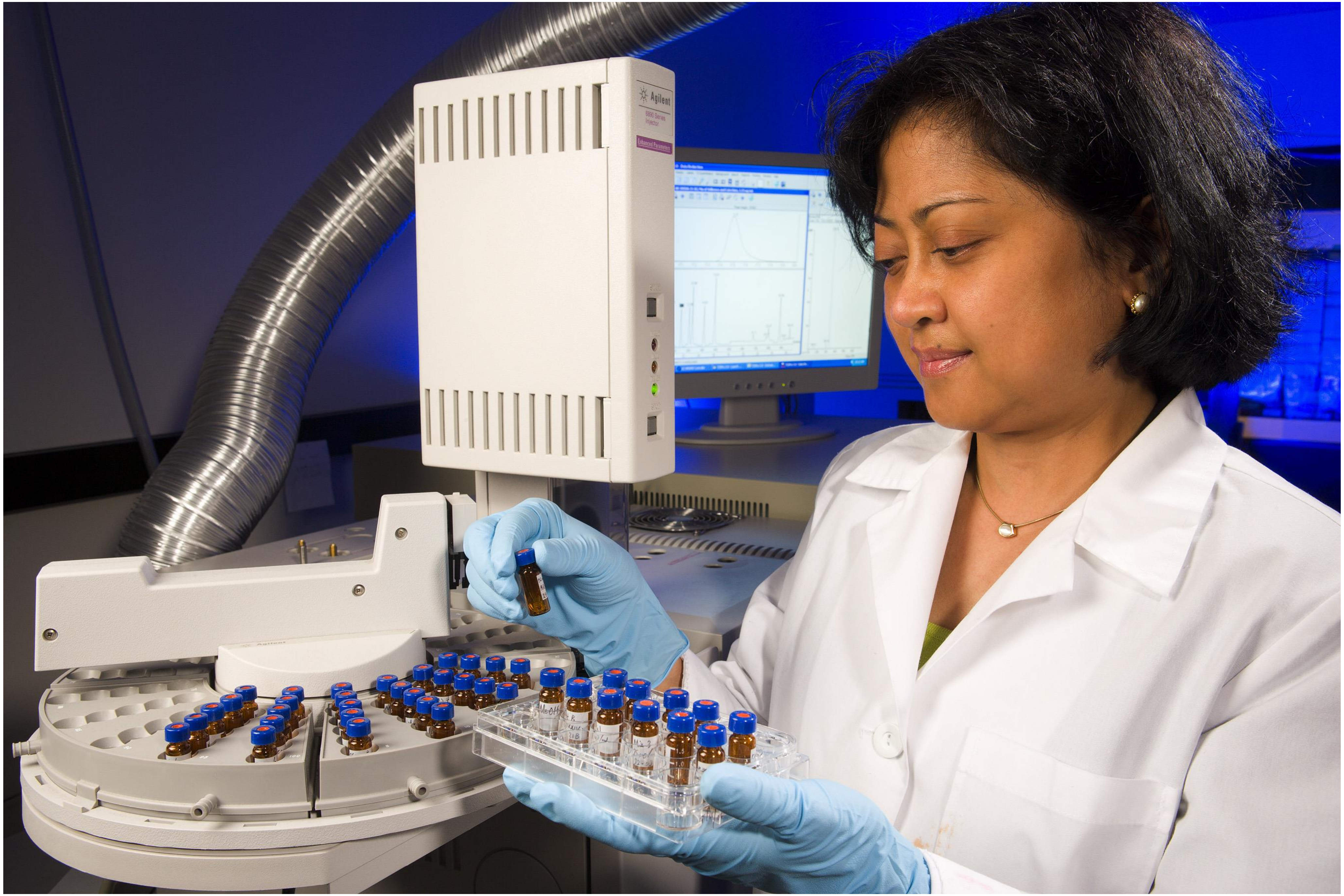
They say scientists work away from the limelight. But they often give society lasting benefits, making life easier, healthier, more comfortable and enjoyable. They find answers and solutions to many of life's questions and problems. We think of Agnes as one of this breed. Certainly we are saddened by her early departure from this world, but probably the Almighty thought she has done enough and it is "mission accomplished" for her. Our family wishfully thinks our dear Agnes has left behind a legacy that gives her a certain measure of immorTality through her research work and service in her adopted country. This week's two ACS symposia in her memory gives her a semblance of such immorTality. Thanks once more to the American Chemical Society for this honor. We know Agnes loved this organization so much. Your gesture gives us great comfort and assuages the pain of our loss and we are forever grateful to all of you.

Thank you all for listening and have a fruitful conference for the rest of the week.

Philip M. Rimando
Manila
21 Aug 2019

AGNES RIMANDO
OCTOBER 17, 1957-JULY 12,2018

Agnes Rimando from UP (University of the Philippines) joined our lab in 1985 as the first foreign student for me, and studied on *Ehretiamicrophylla* (Boraginaceae). She isolated rosmarinic acid as an effective anti-allergic substance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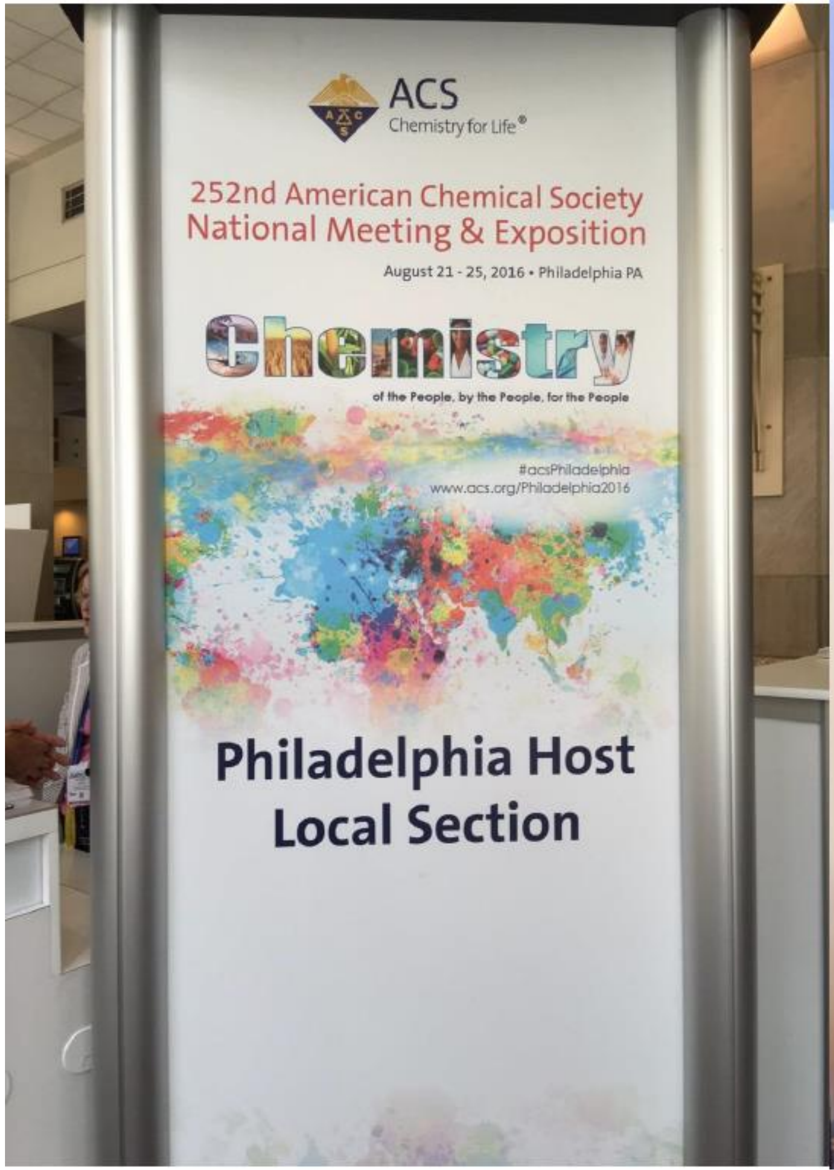
KENNETH SPENCER AWARD FOR ACHIEVEMENT IN AGRICULTURAL CHEMISTRY
ONLY WOMAN AND YOUNGEST RECIPIENT



Dr. Agnes M. Rimando
South Jersey, USDA station, Blueberry Farm

Sincerely,

Agnes M. Rimando, Ph.D.
Research Chemist

AGFD COUNCILORS 2017

USDA JAPAN
NATIONAL FOOD
RESEARCH INSTITUTE
MEETING 2014
NEW ORLEANS

100th ANNIVERSARY

MACHU PICHU, PERU 2016 ACMAP CONFERENCE

7th Annual ACMAP conference, June 27-July 1, 2016, Lima, Peru
Field Trip to Machu Picchu

252 ACS meeting in Philadelphia

August 21-25, 2016

Spencer Award

Dr. Agnes M. Rimando

2015

BOOST Workshop
(Building Opportunity Out of Science and Technology)

2014

1st Joint ACS AGFD – ACS ICSCT Symposium on Agricultural and Food Chemistry

March 4-5, 2014, Bangkok, Thailand

Partners for Progress & Prosperity Award

from ACS President, Marinda Wu
at the ACS National meeting in San Francisco, August 10, 2014

Partners for Progress & Prosperity Award

Presented to

International Chemical Sciences Chapter in Thailand

in recognition of

the successful first joint AGFD – ICSCT Symposium on Agricultural and Food Chemistry in Bangkok, Thailand

Awarded August 10, 2014
248th National ACS Meeting
San Francisco, California, USA

Marinda Li Wu, Ph.D.
2013 ACS President

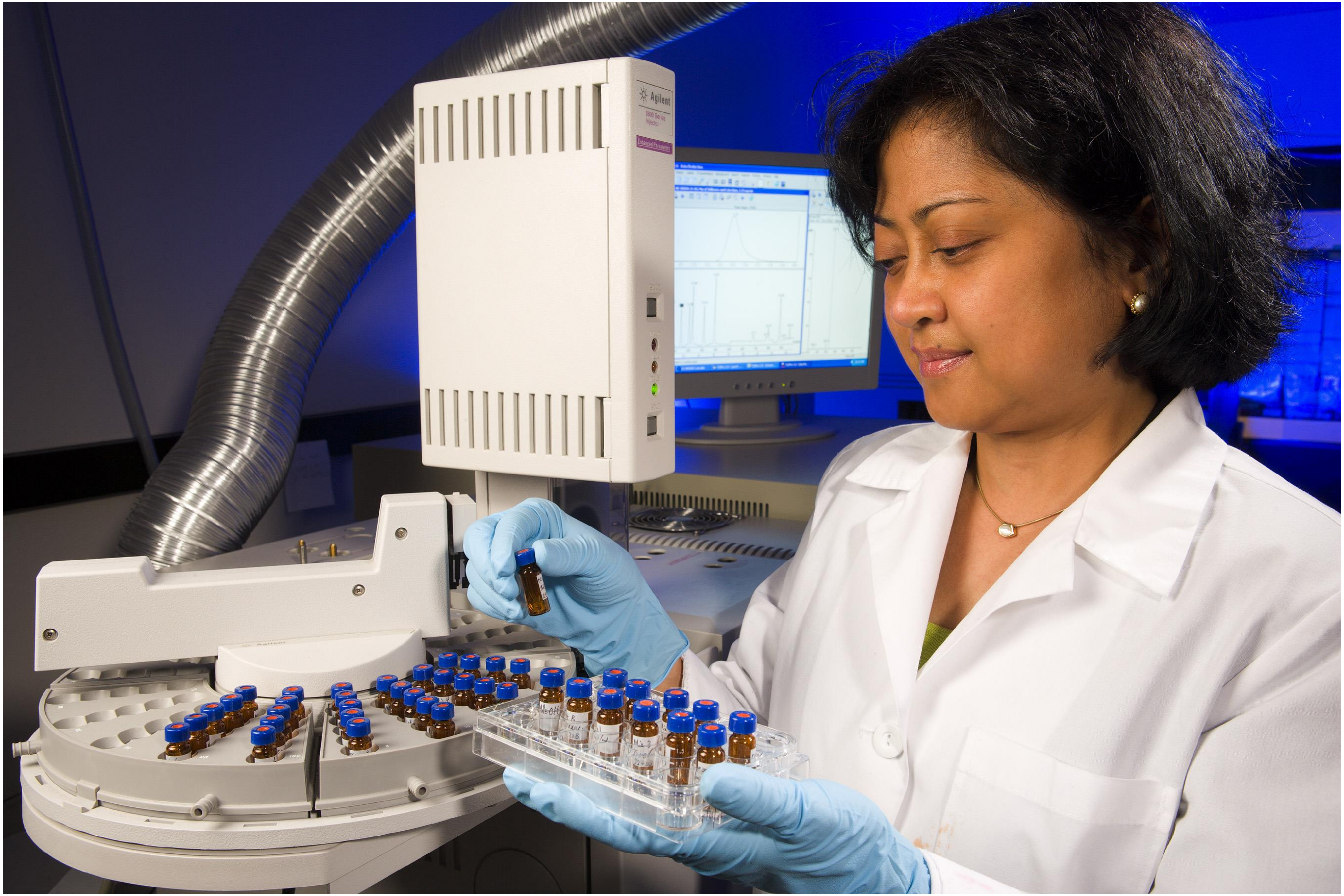
My last picture with Agnes in Jeju, Korea, 2017.

She is my dear friend and always in my memory.

I miss you Agnes!

AGNES RIMANDO
OCTOBER 17, 1957-JULY 12,2018

Agnes Rimando from UP (University of the Philippines) joined our lab in 1985 as the first foreign student for me, and studied on *Ehretiamicrophylla* (Boraginaceae). She isolated rosmarinic acid as an effective anti-allergic substance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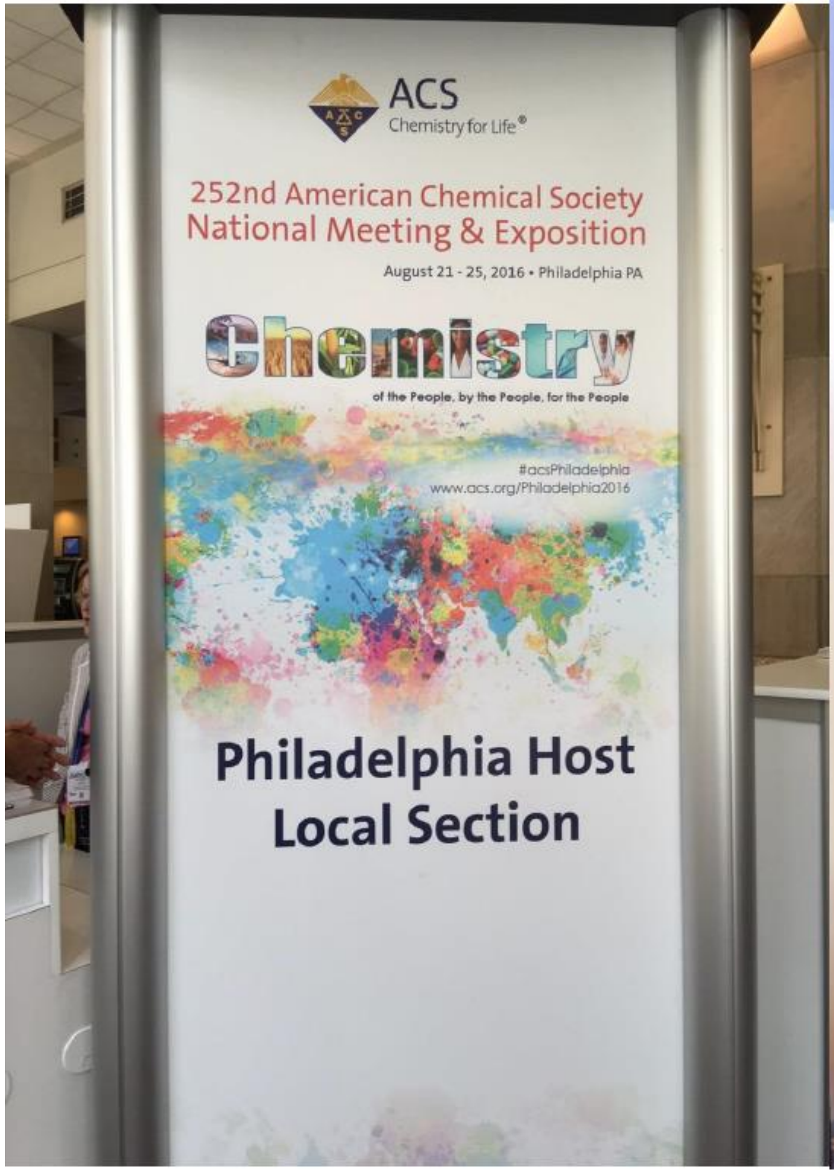
KENNETH SPENCER AWARD FOR ACHIEVEMENT IN AGRICULTURAL CHEMISTRY
ONLY WOMAN AND YOUNGEST RECIPIENT



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Agnes Rimando

A pioneer in the fate of glyphosate and its primary metabolite in plants

John Finley

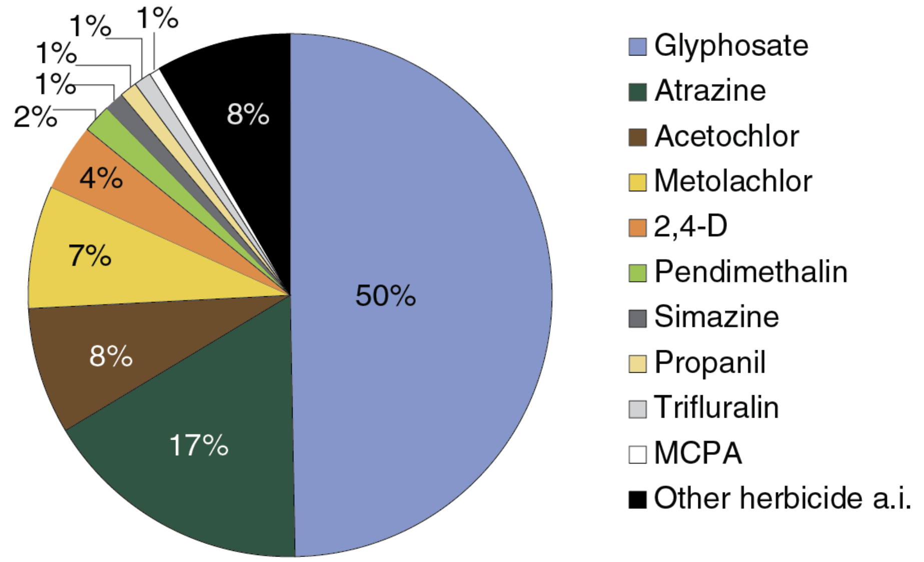
LSU

Stephen O. Duke

USDA

Glyphosate dominates the herbicide market

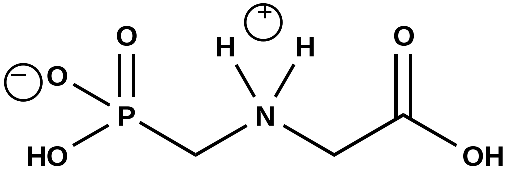
Herbicide use by active ingredient (a.i.), 21 selected crops in 2008, percent total a.i. applied[1]



[1]This graph shows the top herbicide a.i. used in 2008.
Sources: Economic Research Service with USDA and proprietary data. See Appendix 2.

N-phosphonomethylglycine (glyphosate)

- Simple zwitterionic amino acid
- First synthesized in 1950 by Henri Martin (Cilag Co.) for unknown purposes
- Does not fit Tice’s rule for a pesticide
- Chelates metal cations as cytoplasmic pH
- First tested for herbicidal activity by Monsanto Agric. Products in 1970.



Further history

- First marketed by Monsanto in 1974 as a post emergence, non-selective herbicide
- Primarily sold as the isopropylamine salt of the glyphosate anion
- Became a generic pesticide in 2000, after which different formulations and salts of glyphosate became available

Glyphosate Use

- Selective uses
  - Targeted placement
    - Rope wick applicators
    - Recirculating sprayers
    - Hooded sprayers
    - Spot treatments
    - Precision delivery

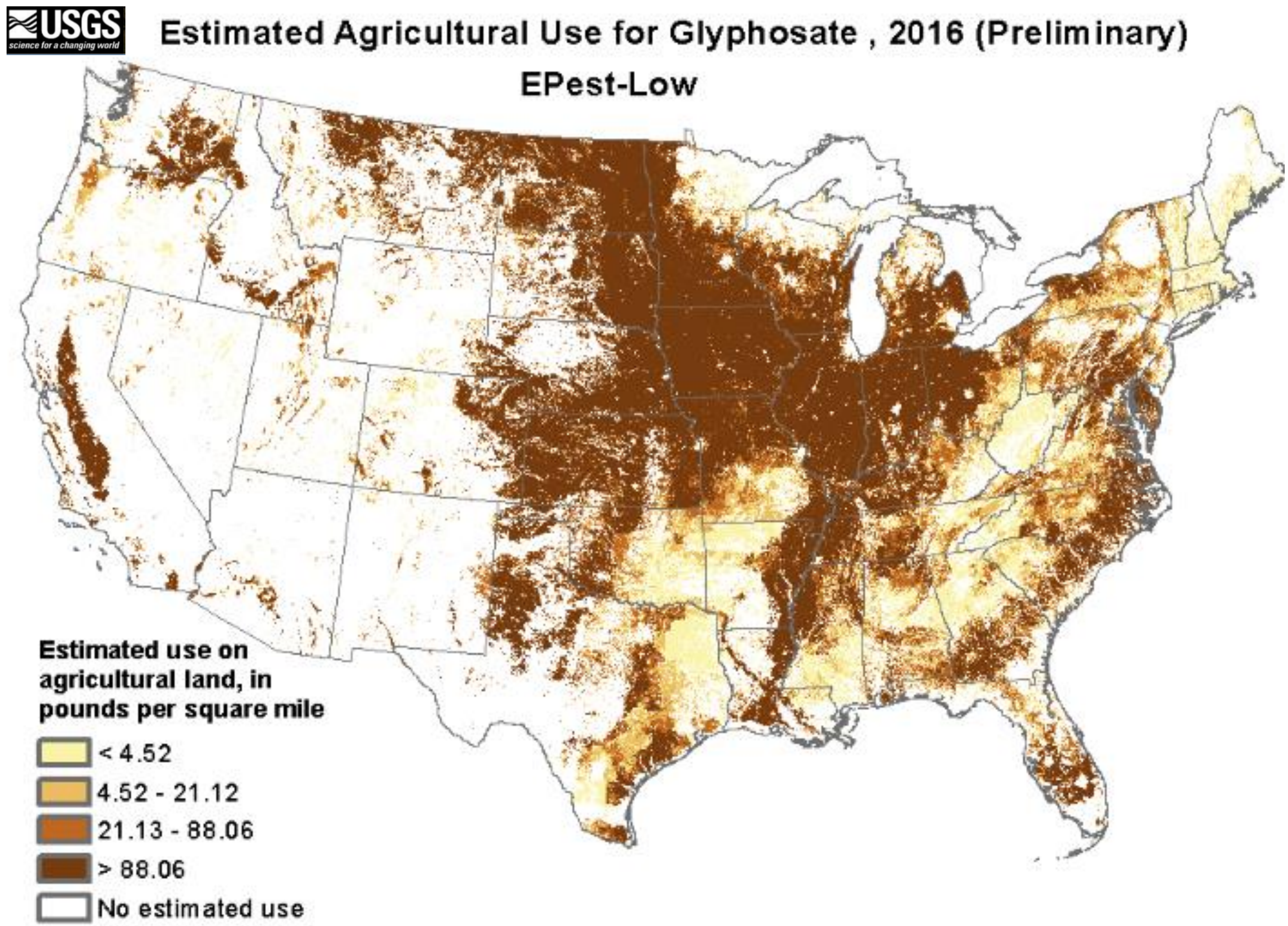
  - Biochemical selectivity
    - Glyphosate-resistant (Roundup Ready®) Crops

Methods for selectivity

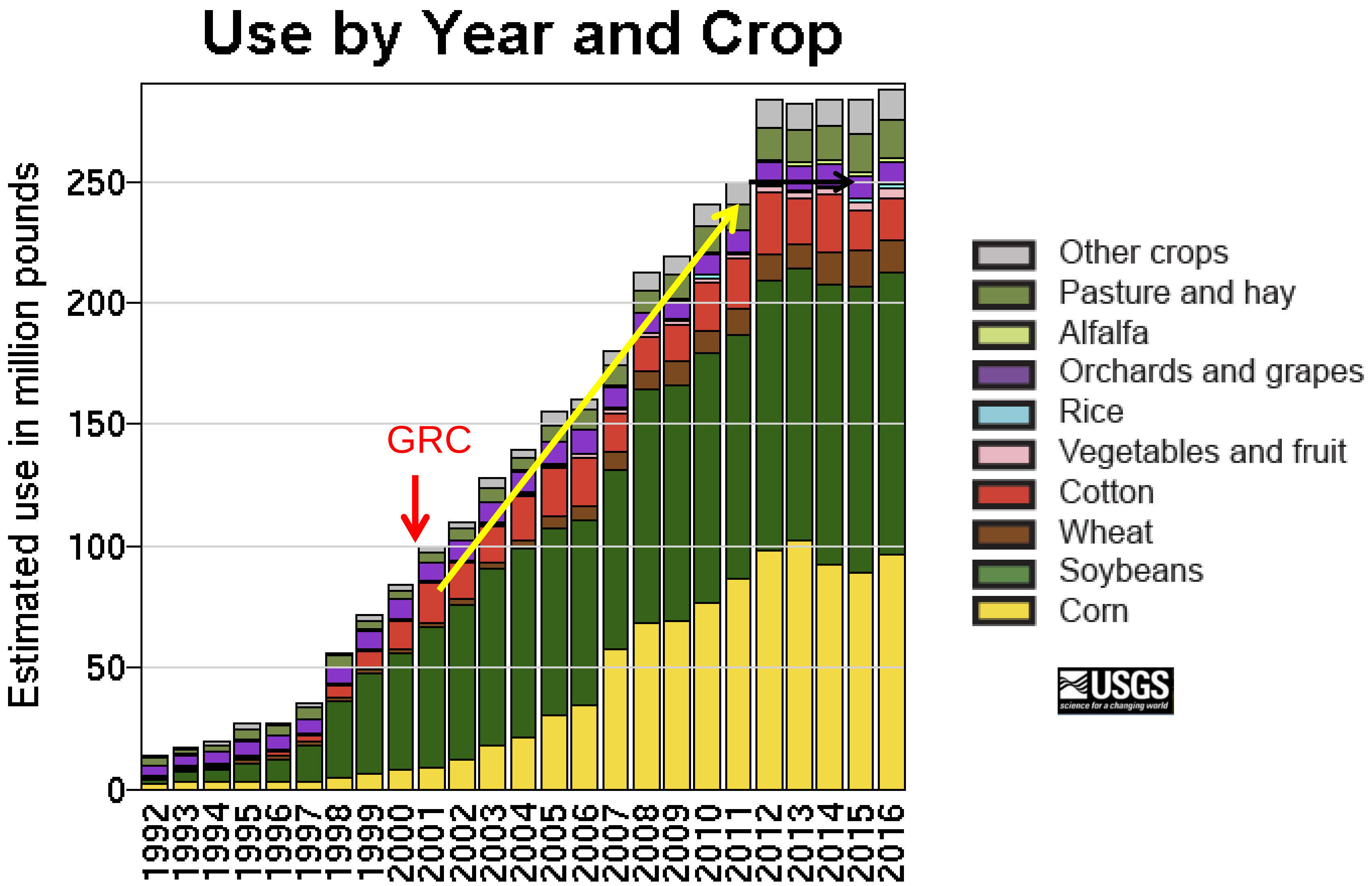
- Directed sprays

Glyphosate-resistant (GR) crops were introduced in 1996

Glyphosate use with a GR soybeans


USGS
science for a changing world
Estimated Agricultural Use for Glyphosate , 2016 (Preliminary)
EPest-Low
Estimated use on agricultural land, in pounds per square mile
< 4.52
4.52 - 21.12
21.13 - 88.06
> 88.06
No estimated use

Glyphosate use in the USA



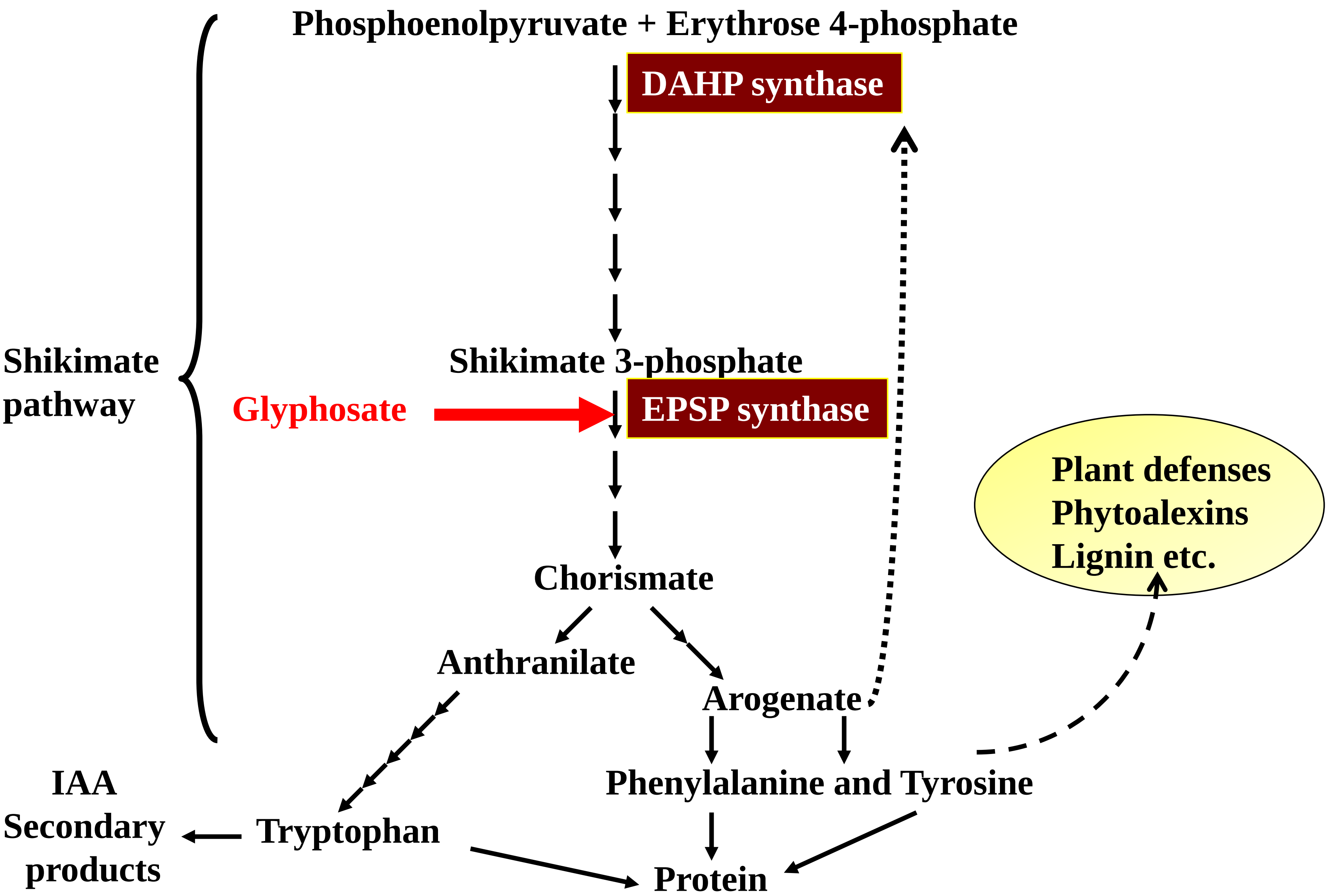
Agnes Rimando's work on this important herbicide

- Showed no effect of glyphosate on estrogenic isoflavone content in GR soybeans
- 1st to publish work on glyphosate metabolism in glyphosate-resistant (GR) crops
- Published only paper comparing glyphosate metabolism in an array of plant species
- Found no role of enhanced glyphosate metabolism in evolved GR weeds or on natural tolerance of weeds
- Generated data to indicate the "yellow flash" of GR soybeans is due to accumulation of AMPA, the major degradation product of glyphosate
- Published only papers on glyphosate metabolism in GR canola

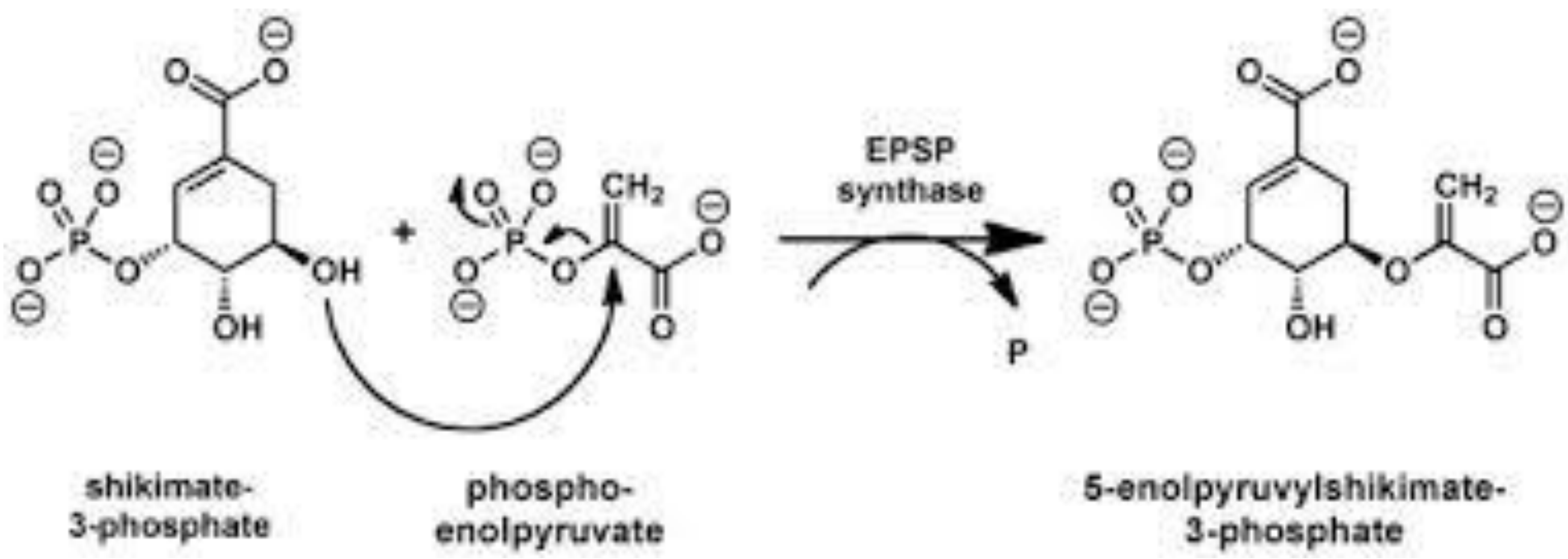
Effects of glyphosate on estrogenic isoflavone levels in glyphosate-resistant (GR) soybeans

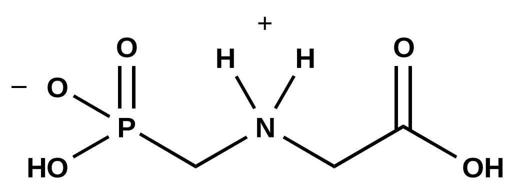
- Lappe´, M. A.; Bailey, E. B.; Childress, C.; Setchell, K. D. R. Alterations in clinically important phytotestrogens in genetically modified, herbicide-tolerant soybeans. *J. Med. Foods* **1999**, *1*, 241-245.
- This paper reported reductions of these phytochemicals in GR soybeans.
- But, they did not do the work with isogenic lines, so the paper was inconclusive.
- But glyphosate used on these cultivars might reduce levels of these compounds because of its mode of action through the shikimic pathway

Mechanism of action of glyphosate



EPSP Synthase





Glyphosate

- A study was instituted to examine this, using two different GR soybean variety at two different field sites (Mississippi and Missouri).

- Glyphosate was appliced at the highest allowable field rate (1.26 kg/ha a.i.) and latest application time (full flowering)

340 *J. Agric. Food Chem.* **2003,** *51,* 340–344

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Isoflavone, Glyphosate, and Aminomethylphosphonic Acid Levels in Seeds of Glyphosate-Treated, Glyphosate-Resistant Soybean

Stephen O. Duke,*,† Agnes M. Rimando,† Patrick F. Pace,† Krishna N. Reddy,‡ and Reid J. Smeda§

Found no effects on any estrogenic isoflavones

Shikimate and isoflavone contents of harvested seed in Mississippi

Compound	Control	Glyphosate treatment (µg/g)
Shikimate	52	55
Daidzein	1023	883
Daidzin	1102	973
Genistein	258	147
Genistin	1136	1105
Glycitein	973	806
Glycitin	383	394

No significant effects

Shikimate and isoflavone contents of harvested seed in Missouri (different cultivar)

Compound	Control	Glyphosate treatment
	(µg/g)	
Shikimate	29	60
Daidzein	805	967
Daidzin	1367	1704
Genistein	250	389
Genistin	1403	1347
Glycitein	973	806
Glycitin	583	556

No significant effects

- This is not surprising since there was no increase in shikimate, and this is the best biomarker for inhibition of the shikimate pathway.

- But to have an effect on the shikimate pathway, the glyphosate must be in the seed, translocated from the leaves.

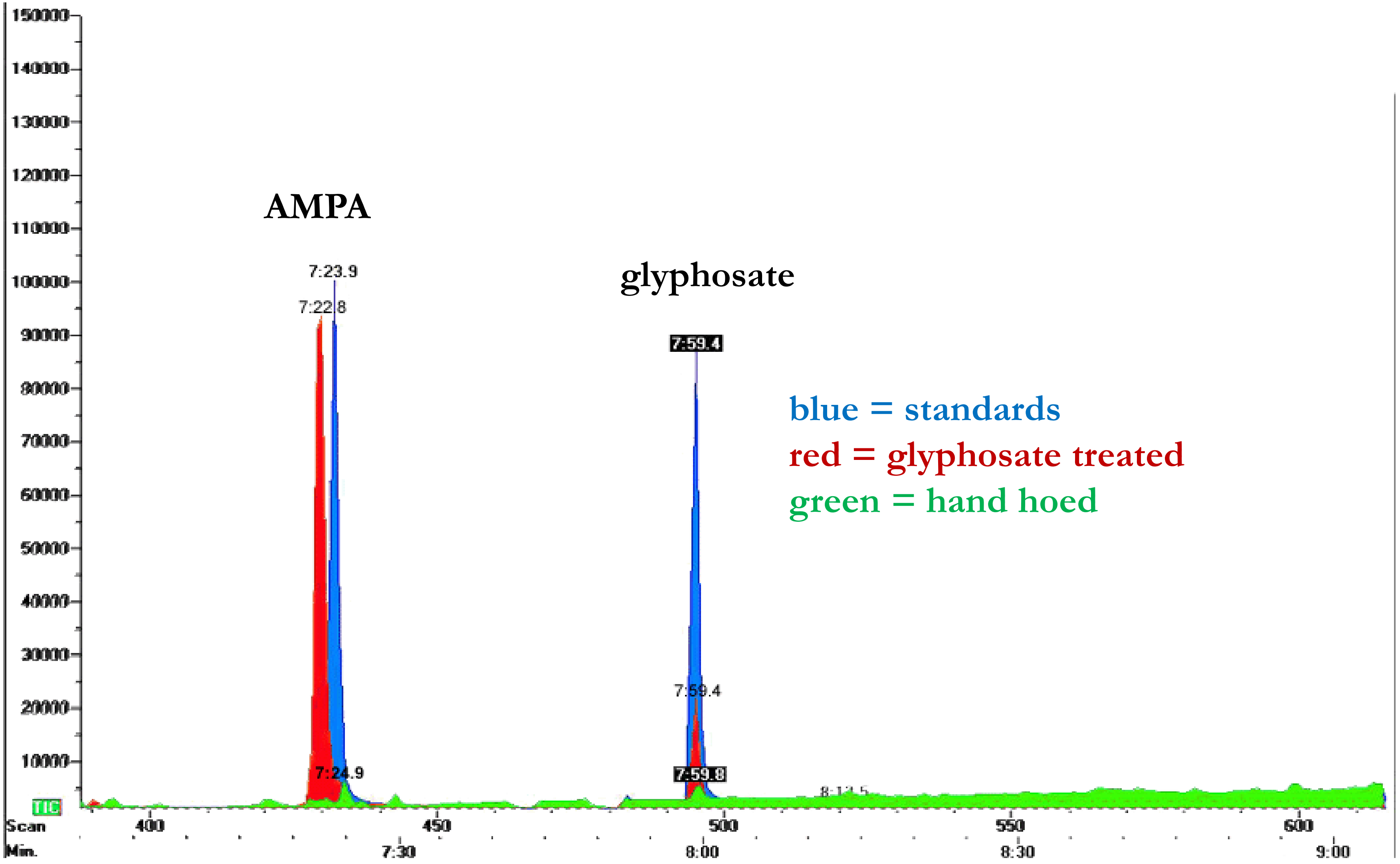
Glyphosate (ng/g)* of seeds

Treatment	MS	MO
Hand weeded	**181b**	**234b**
Glyphosate	**2175a**	**3080a**

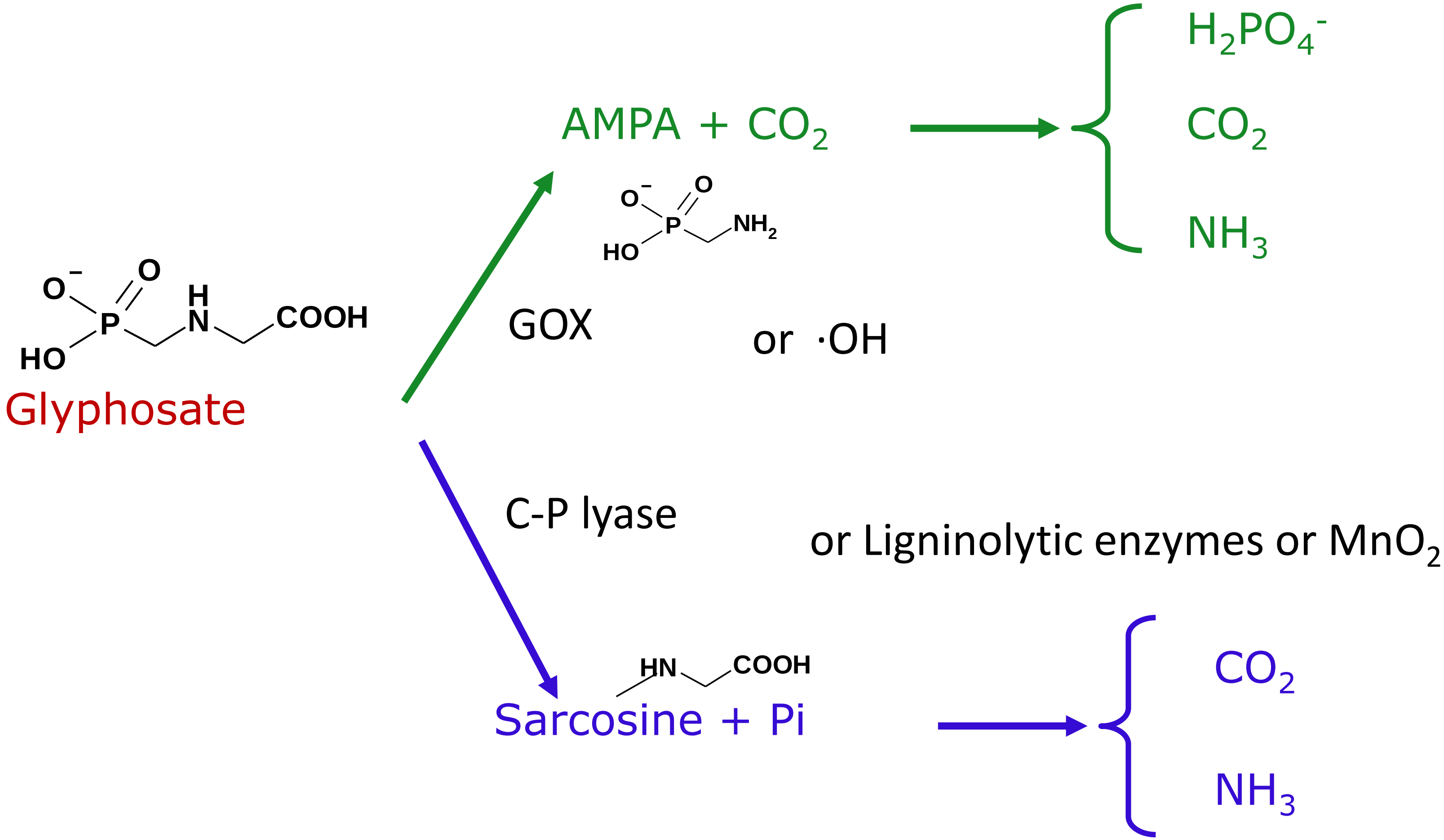
*** USEPA tolerance limit is 20,000 ng/g**

Duke *et al.*, *J. Agric. Food Chem.* 51:340-4 (2003)

GS/MS


AMPA
glyphosate
blue = standards
red = glyphosate treated
green = hand hoed
7:23.9
7:22.8
7:24.9
7:59.4
7:59.4
7:59.8
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
TIC
Scan
Min.
400
450
500
550
600
7:30
8:00
8:30
9:00

Two enzymatic degradation pathways known to microbes



AMPA (ng/g)* of seeds

Treatment	MS	MO
Hand weeded	**602b**	**862b**
Glyphosate Treated	**7256a**	**25005a**

Duke *et al.*, *J. Agric. Food Chem.* 51:340-4 (2003)

Similar results on accumulation of glyphosate and AMPA in GR soy seeds were later reported by others:

- Bohm GMB, Rombaldi CV, Genovese MI, Castilhos D, Alves BJR, Rumjanek NG. 2014. Glyphosate effects on yield, nitrogen fixation, and seed quality in glyphosate-resistant soybean. *Crop Sci.* 54:1737-1743.

- Bøhn T, Cuhra M, Traavik T, Sanden M, Fagan J, Primicerio R. 2014. Compositional differences in soybeans on the market: glyphosate accumulates in Roundup Ready GM soybeans. *Food Chem*. 153:207-215.

Much less glyphosate and no AMPA found in seed of GR maize

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

Cite This: J. Agric. Food Chem. 2018, 66, 10139−10146

pubs.acs.org/JAFC

Glyphosate Resistance Technology Has Minimal or No Effect on Maize Mineral Content and Yield

Krishna N. Reddy,[†] James V. Cizdziel,[‡] Martin M. Williams, II,[§] Jude E. Maul,[||] Agnes M. Rimando,[⊥] and Stephen O. Duke[*,⊥]

Mississippi – 0.87 kg/ha X2 sequentially
Urbana – 1.68 kg/ha at V4-5 stage

No glyphosate or AMPA found in seed in 2013 or 2014 in Mississippi or in 2013 in Illinois

In 2014, 25 and 41 ng/g of glyphosate were found in seed of no glyphosate history and no glyphosate history fields, respectively

Similar results have come from Brazil

Glyphosate content of GR maize seed

Treatment	ng/g
Control	ND
Gly 2X[a]	0.12
Gly 1X – 0.98 kg at 21 DAE	ND

[a]0.52 and 0.98 kg at 14 and 28 DAE

Costa et al. 2018. *GM Crops & Food* 9: DOI: 10.1080/21645698.2018.1511204

Published only paper comparing glyphosate metabolism in an array of plant species:

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

J. Agric. Food Chem. **2008,** *56,* 2125–2130 **2125**

Aminomethylphosphonic Acid Accumulation in Plant Species Treated with Glyphosate

KRISHNA N. REDDY,[*,†] AGNES M. RIMANDO,[‡] STEPHEN O. DUKE,[‡] AND VIJAY K. NANDULA[§]

Effects of an I_{50} dose of glyphosate on AMPA levels in shoots 7 days after application

Species	I_{50}	glyphosate	AMPA	glyphosate/AMPA
	g ae/ha	— ng/g of tissue —		
Soybean	250	25,000	670	38
Cowpea	201	26,800	4,770	6
Sicklepod	252	6,410	1,930	4
Coffee Senna	75	5,900	287	21
Hemp sesbania	456	38,700	nd	-
Ill bundle flower	272	3,270	1,510	2
Kudzu	77	5,560	297	19
Velvetleaf	122	678	nd	-
Horseweed	170	26,300	314	84
Corn	93	308	nd	-
Ryegrass	220	7,432	nd	-

Found no role of enhanced glyphosate metabolism in evolved GR weeds or on natural tolerance of weeds to glyphosate

Nandula, V.K., K.N. Reddy, D.H. Poston, A.M. Rimando, and S.O. Duke. 2008. Glyphosate tolerance mechanism in Italian ryegrass (*Lolium multiflorum*) from Mississippi. *Weed Sci.* 56: 344-349.

Nandula, V.K., K.N. Reddy, C.H. Koger, D.H. Poston, A.M. Rimando, S.O. Duke, J.A. Bond, and D.N. Ribeiro. 2012. Multiple resistance to glyphosate and pyrithiobac in Palmer amaranth (*Amaranthus palmeri*) from Mississippi and response to flumiclorac. *Weed Sci.* 60:179-188.

Ribiero, D.N., V.K. Nandula, F.E. Dayan, A.M. Rimando, S.O. Duke, K.N. Reddy, and D.R. Shaw. 2015. Possible glyphosate tolerance mechanism in pitted morningglory (*Ipomoea lacunosa*). *J. Agric. Food Chem*. 63:1689-1697.

"Yellow flash" is a phenomenon found under some environmental conditions when GR soybeans are sprayed with glyphosate

Soybean yellow flash injury, 3 d after 2nd POST

Glyphosate ((Roundup Ultra)
Rate: 0.84 kg ae/ha, twice
Variety: DP5806RR
Date: June 15, 2000

Years earlier, Robert Hoagland had shown that AMPA is phytotoxic.

Agnes generated data to indicate the “yellow flash” of GR soybeans treated with glyphosate is due to high accumulation of AMPA, the major degradation product of glyphosate.

Summary of Reddy *et al.*, *J. Agric. Food Chem*. 52: 5139-5143 (2004):

- Similar AMPA levels in glyphosate-treated GR soybean and AMPA-treated GR and non-GR soybean were associated with similar injury.

- This supports the hypothesis that the mild injury sometimes seen with glyphosate in soybeans is due to AMPA toxicity.

All GR crops contain a transgene for a resistant form of EPSPS, the target enzyme of glyphosate.

But, GR canola also contained a transgene for a microbial glyphosate oxidotreductase (GOX) that converts glyphosate to AMPA.

Agnes is the only chemist to have published papers on the rapid metabolism of glyphosate to AMPA in GR canola.

GOX is no longer used in GR canola.

3540 *J. Agric. Food Chem.* **2007,** *55,* 3540–3545

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Glyphosate-Resistant and -Susceptible Soybean (*Glycine max*) and Canola (*Brassica napus*) Dose Response and Metabolism Relationships with Glyphosate

VIJAY K. NANDULA,*,† KRISHNA N. REDDY,‡ AGNES M. RIMANDO,§ STEPHEN O. DUKE,§ AND DANIEL H. POSTON†

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

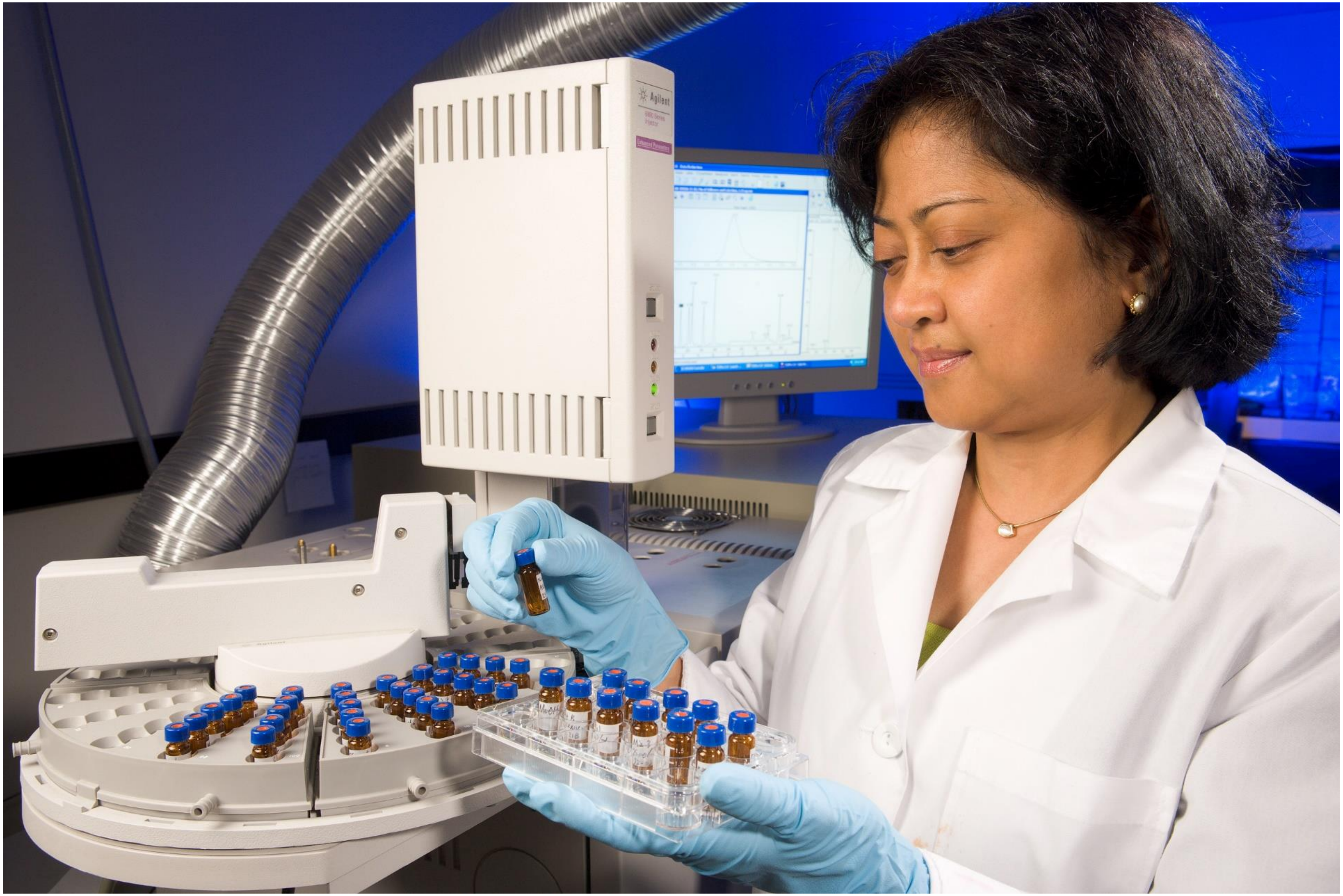
Article

pubs.acs.org/JAFC

Glyphosate-Resistant and Conventional Canola (*Brassica napus* L.) Responses to Glyphosate and Aminomethylphosphonic Acid (AMPA) Treatment

Elza Alves Corrêa,† Franck E. Dayan,§ Daniel K. Owens,§ Agnes M. Rimando,§ and Stephen O. Duke*,§

Glyphosate metabolism - another facet of the accomplishments of Agnes Rimando’s impressive career



Thanks for listening

USDA

Agnes Rimando’s studies of sorgoleone, a weed-fighting quinone

Stephen O. Duke, Zhiang Pan, Franck E. Dayan, and Scott R. Baerson

Natural Products Utilization Research Unit

National Center for Natural Products Research

United States Department of Agriculture – Agricultural Research Service

ACS – August 27, 2019

Phytochemistry 71 (2010) 1032–1039

ELSEVIER

Contents lists available at ScienceDirect

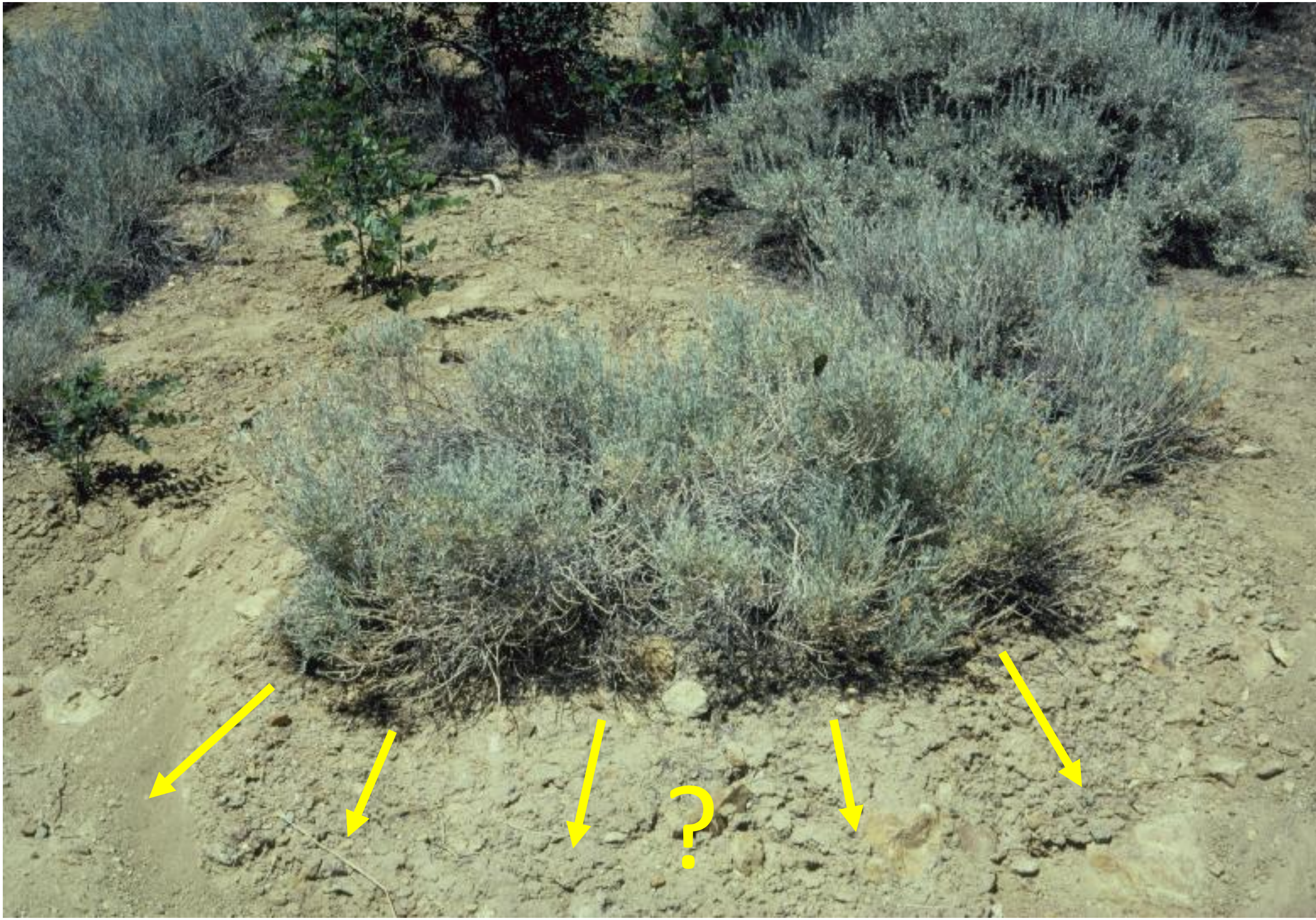
Phytochemistry

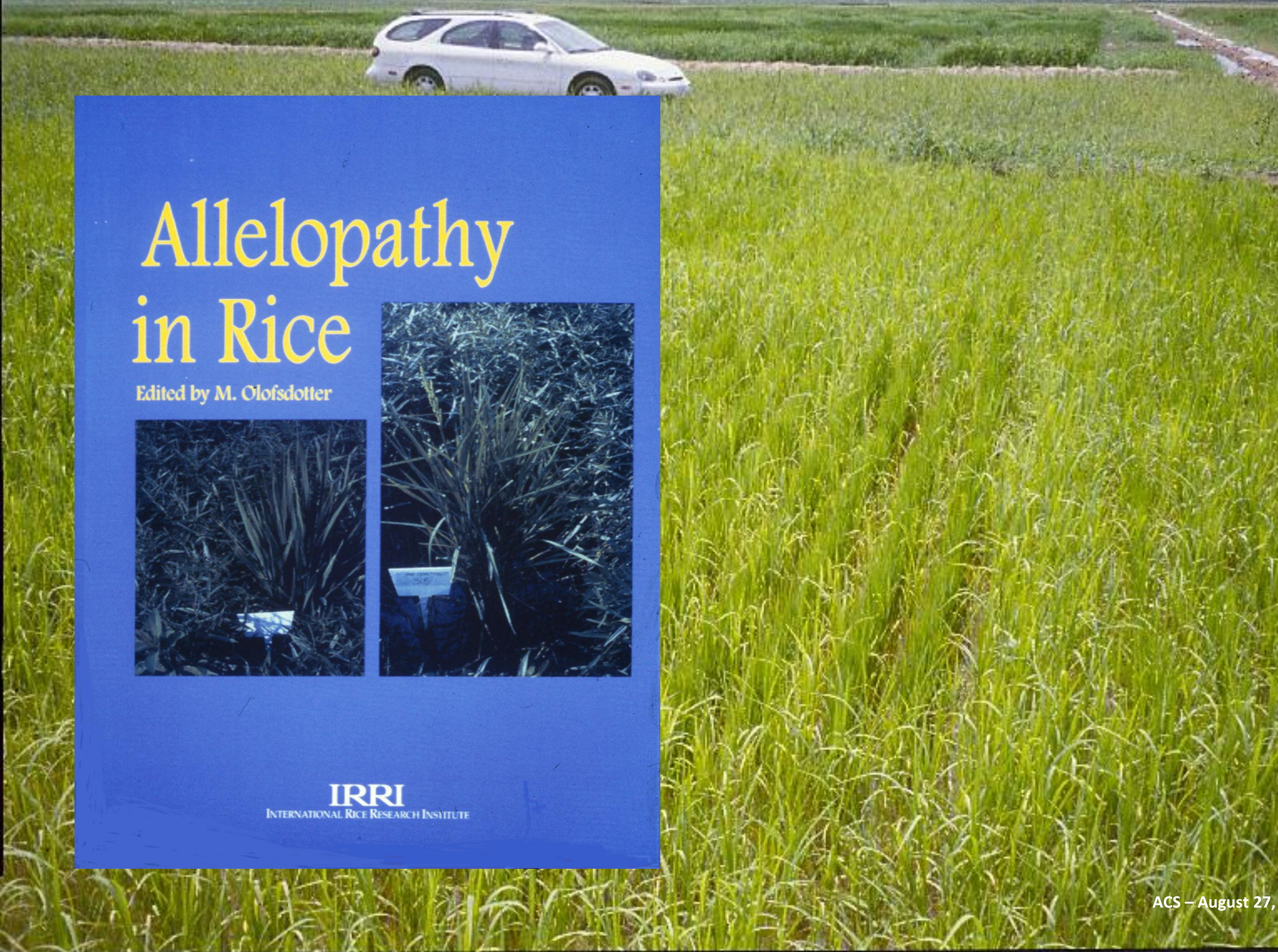
journal homepage: www.elsevier.com/locate/phytochem

Molecules of Interest

Sorgoleone

Franck E. Dayan [a,*], Agnes M. Rimando [a], Zhiqiang Pan [a], Scott R. Baerson [a], Anne Louise Gimsing [b], Stephen O. Duke [a]



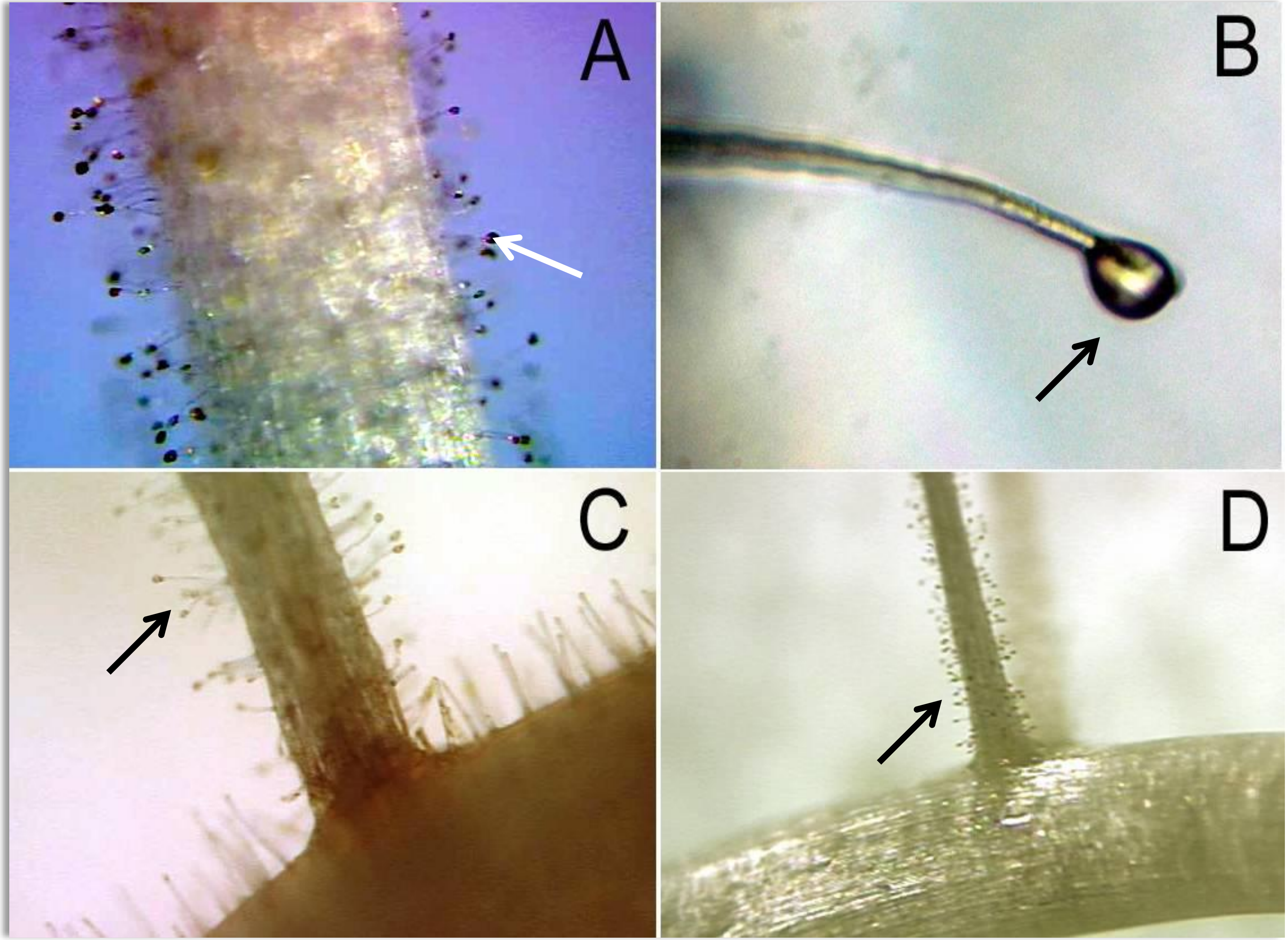

Allelopathy in Rice
Edited by M. Olofsdotter
IRRI
International Rice Research Institute
ACS – August 27,

Transgenes to Improve Allelopathy

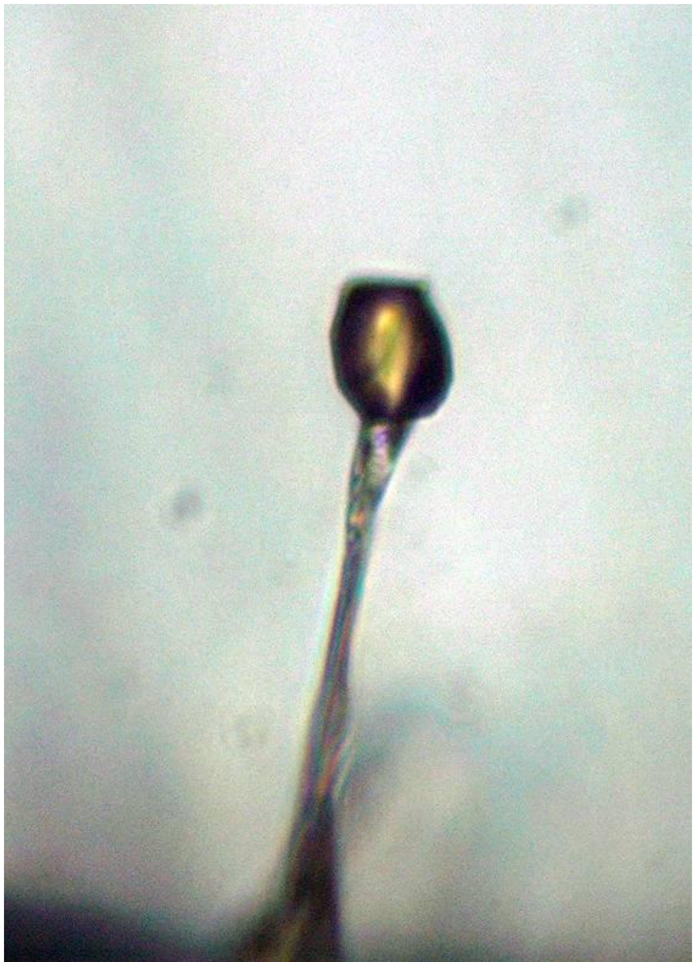
- Root-specific, exuded
- Crop must be resistant
- Highly phytotoxic

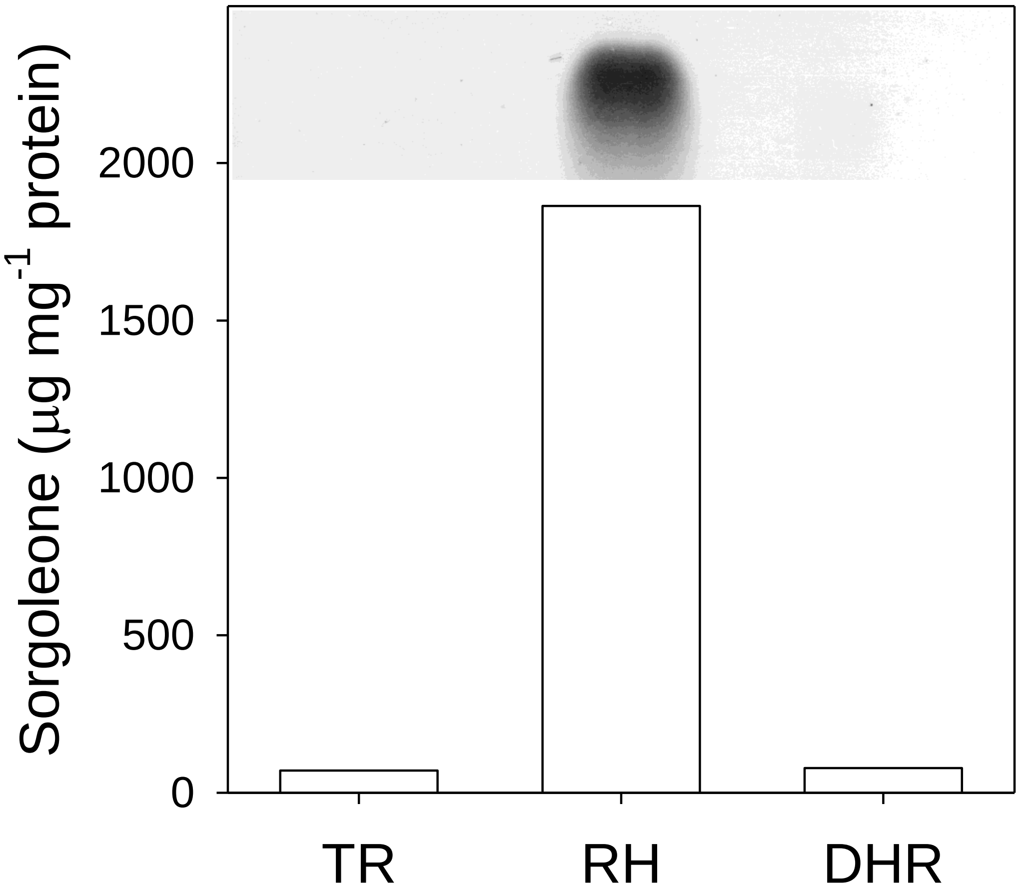
USDA

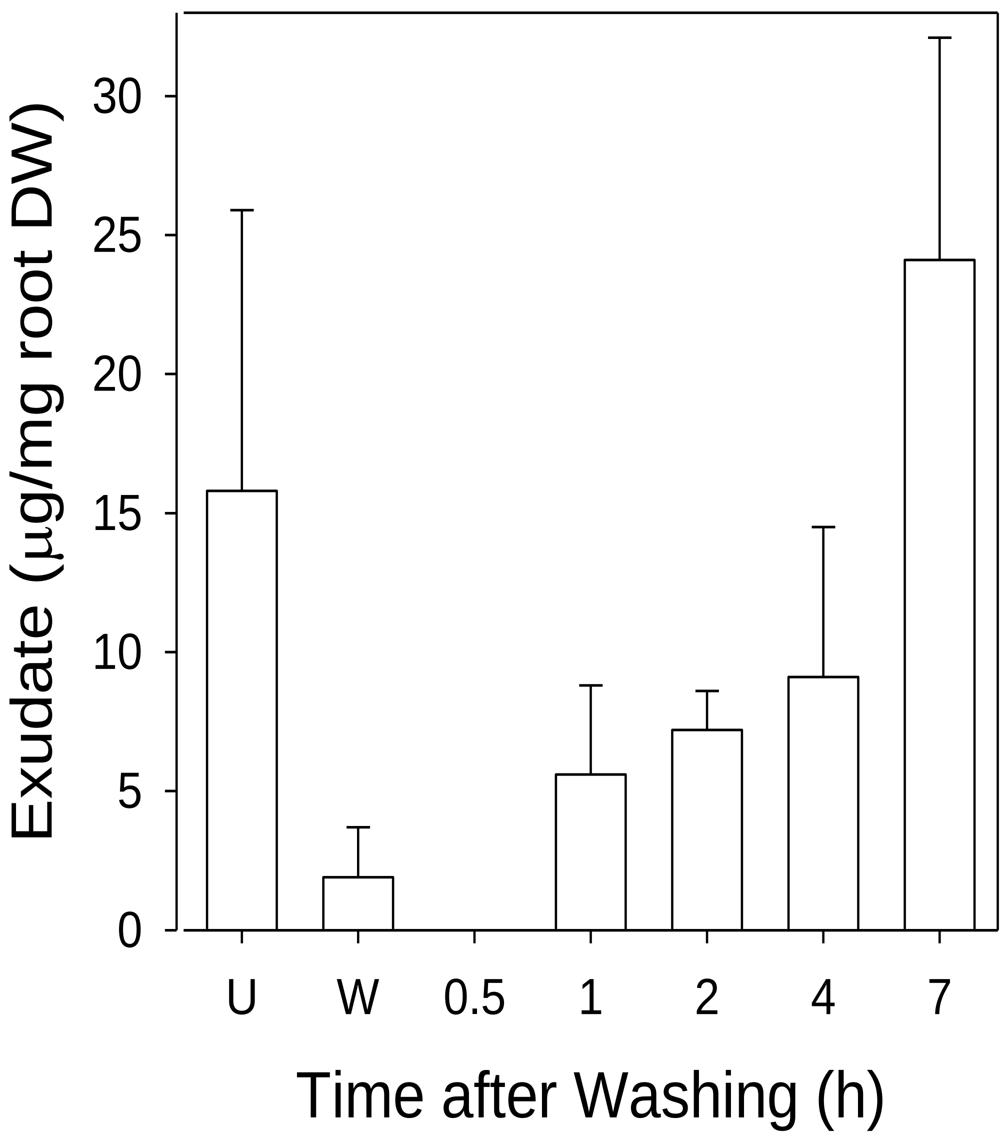
United States Department of Agriculture – Agricultural Research Service


A
B
C
D

Tissue compartmentalization







Synthetic flux

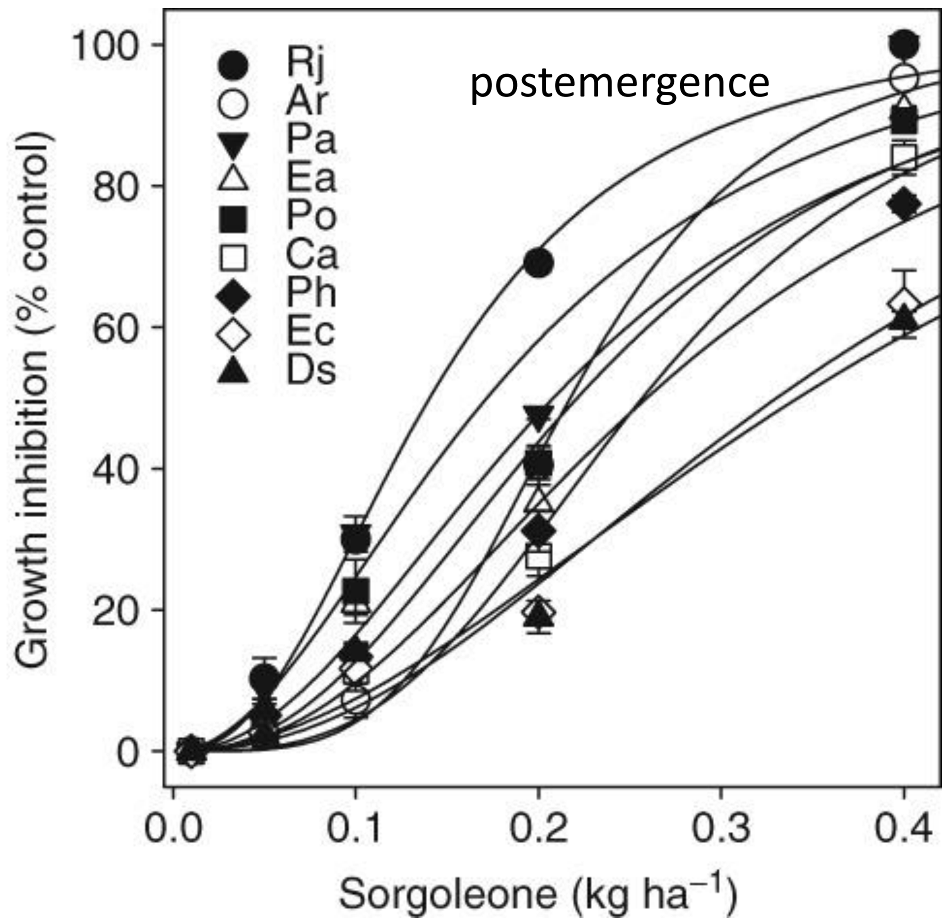
Dayan 2006 Factors modulating the levels of the allelochemical sorgoleone in *Sorghum bicolor*. Planta 224: 339-346.

Effects of a foliar application of 0.6 kg/ha of sorgoleone to various weeds 10 days after application

Weed	Fresh wt. reduction (%)
Nightshade	90
Pigweed	82
Lamsquarters	26
Common ragweed	88
Giant foxtail	12
Sicklepod	60
Common purslane	53
Large crabgrass	43
Velvetleaf	40

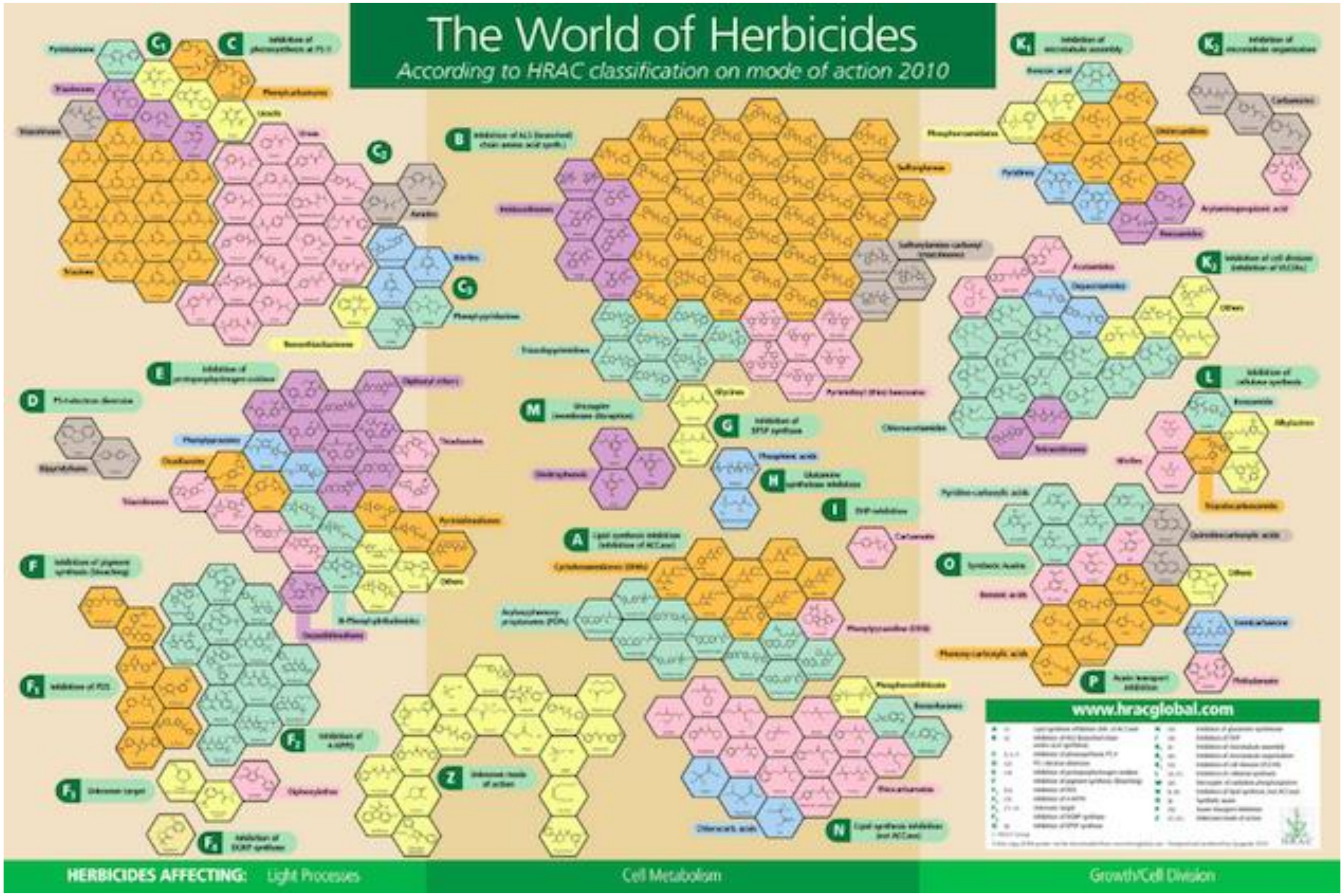
Mark Czarnota dissertation (Cornell Univ.), 2001

Herbicidal activity of formulated (4.6% WP) sorgoleone on several weed species

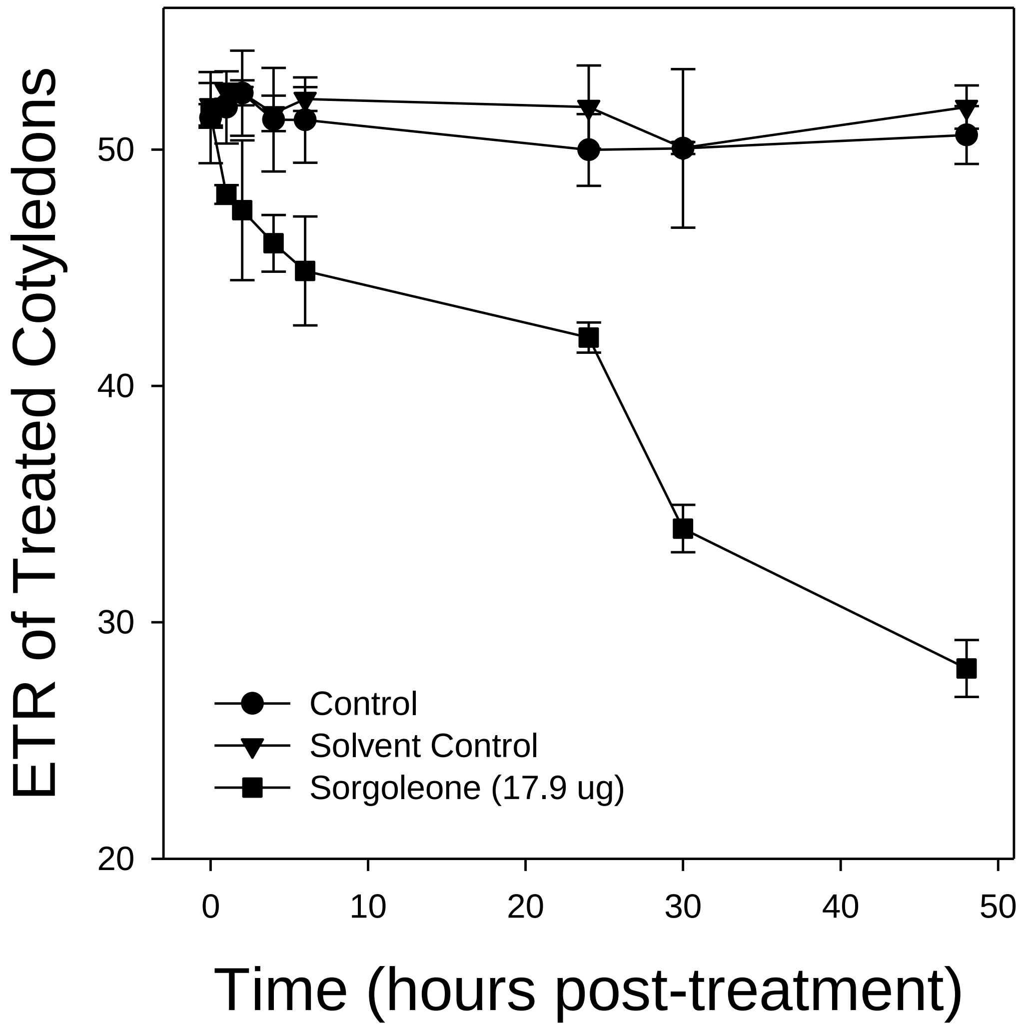


Uddin et al., Pest Management Science, Volume: 70, Issue: 2, Pages: 252-257, First published: 05 April 2013, DOI: (10.1002/ps.3550)

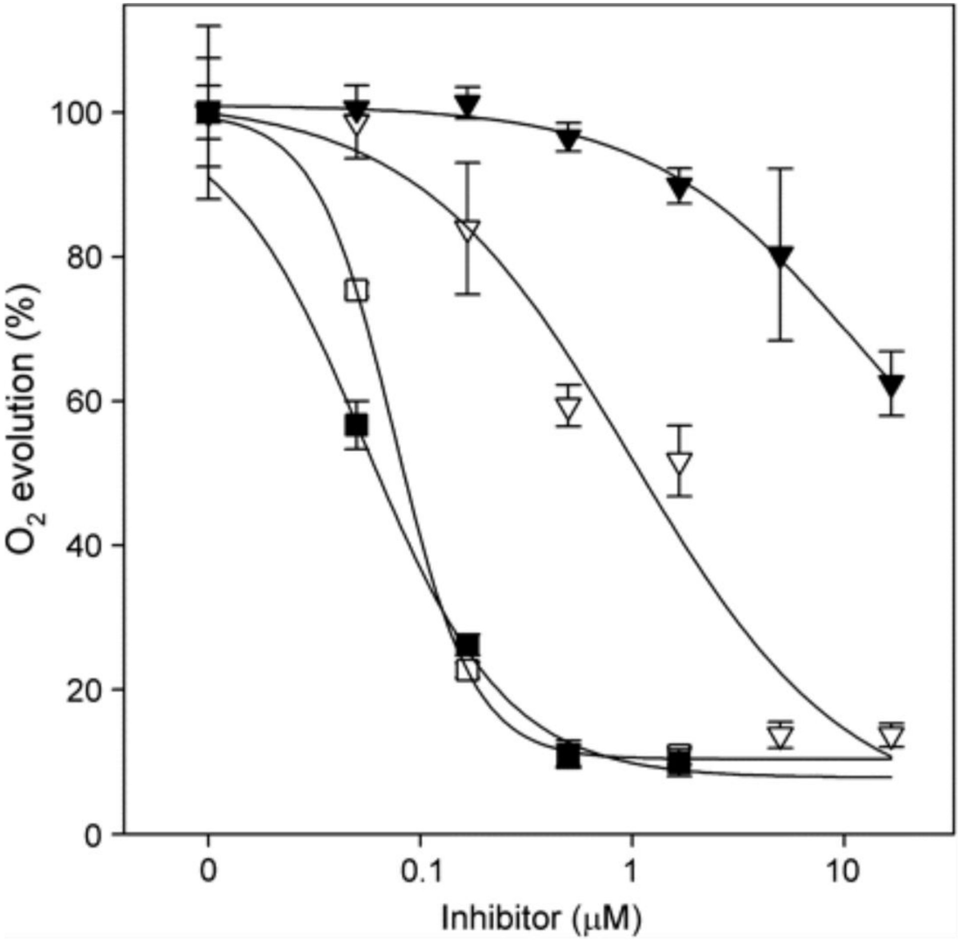
Mode of action



100 µM sorgoleone on velvetleaf cotyledon



Dayan et al. 2009 Dynamic root exudation of sorgoleone and its *in planta* mechanism of action. J Exp Bot 60: 2107-2117.



Squares = sorgoleone

Triangles = atrazine

Filled = triazine resistant

Open = triazine susceptible

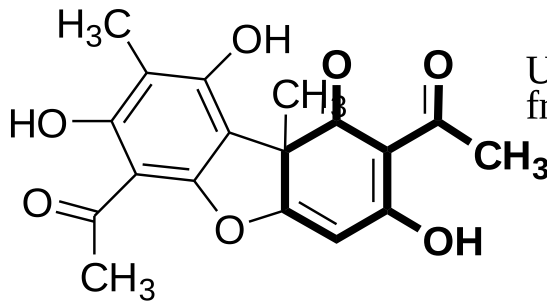
Journal of Experimental Botany, Volume 60, Issue 7, 08 April 2009, Pages 2107–2117, https://doi.org/10.1093/jxb/erp082

Effects of various quinones and cyanide on respiration of isolated potato mitochondria

Quinone	I_{50} (µM)
Anthraquinone	> 100
p-benzoquinone	> 100
Juglone	> 100
Lapachnol	11.5
2-hydroxyl-3-(5-methylhexyl)-4,4-naphthoquinone	6.0
Sorgoleone	8.0
Cyanide	8.0

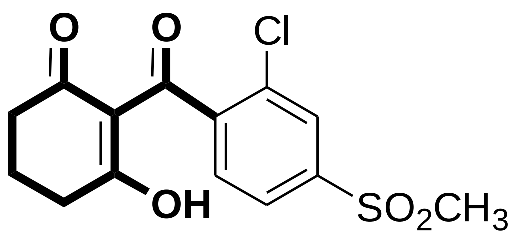
Mark Czarnota dissertation (Cornell Univ.), 2001

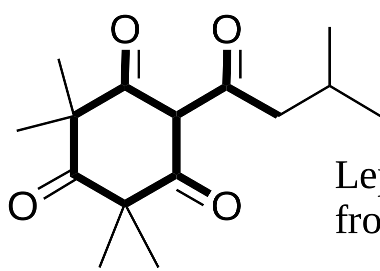
Structural similarities with HPPD inhibitors



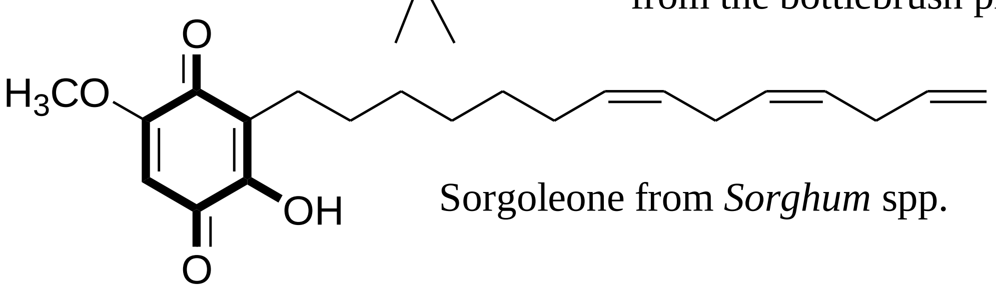
Usnic acid
from lichens

Sulcotrione

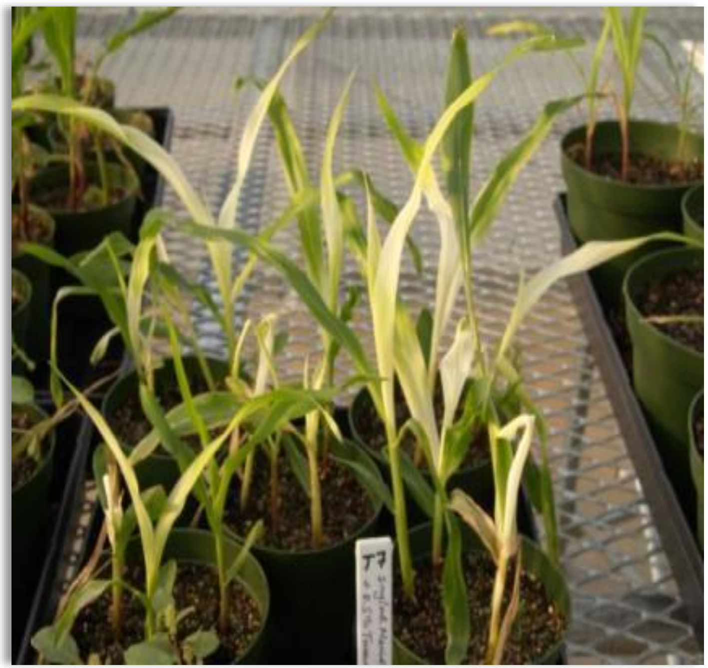


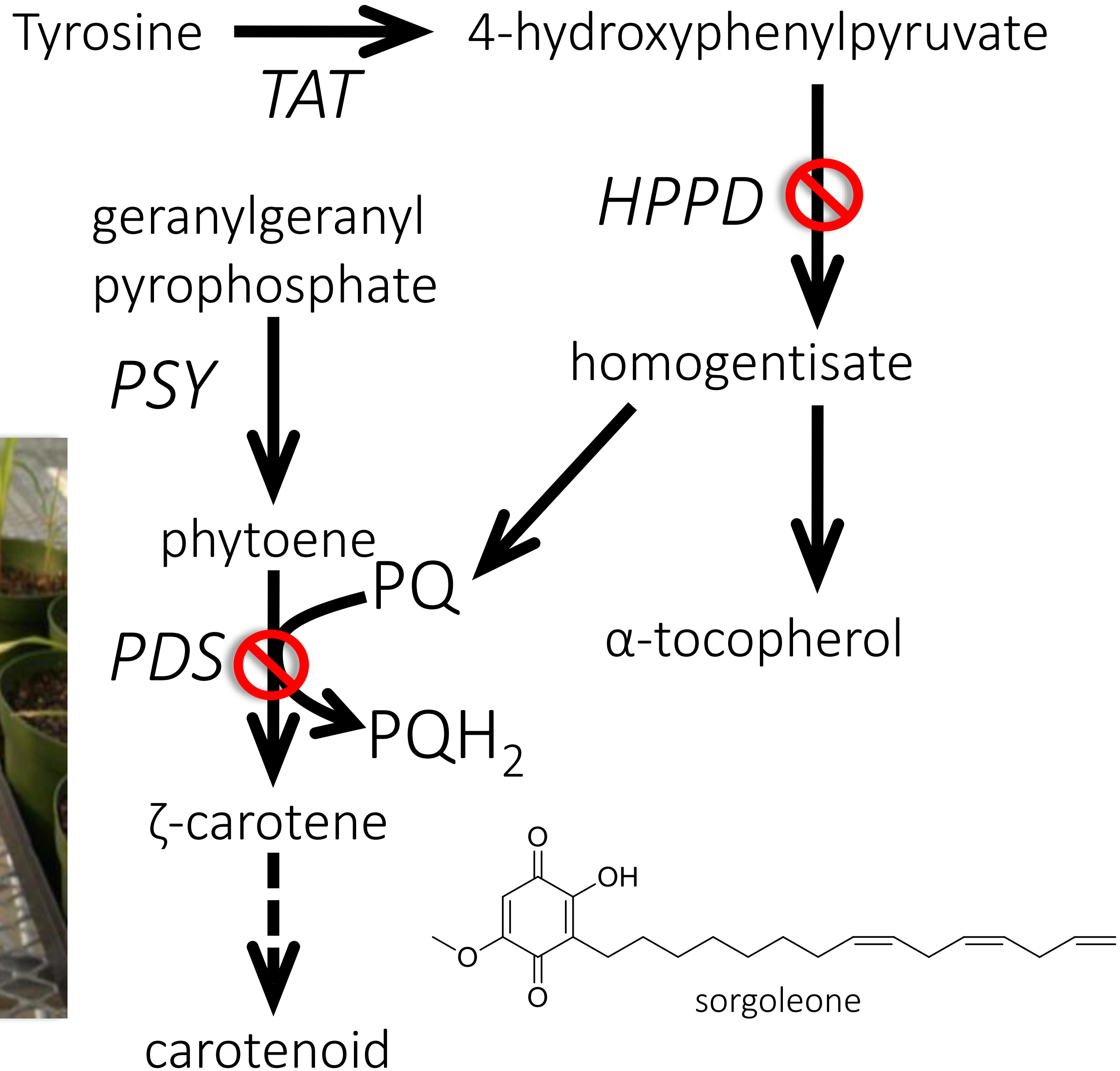


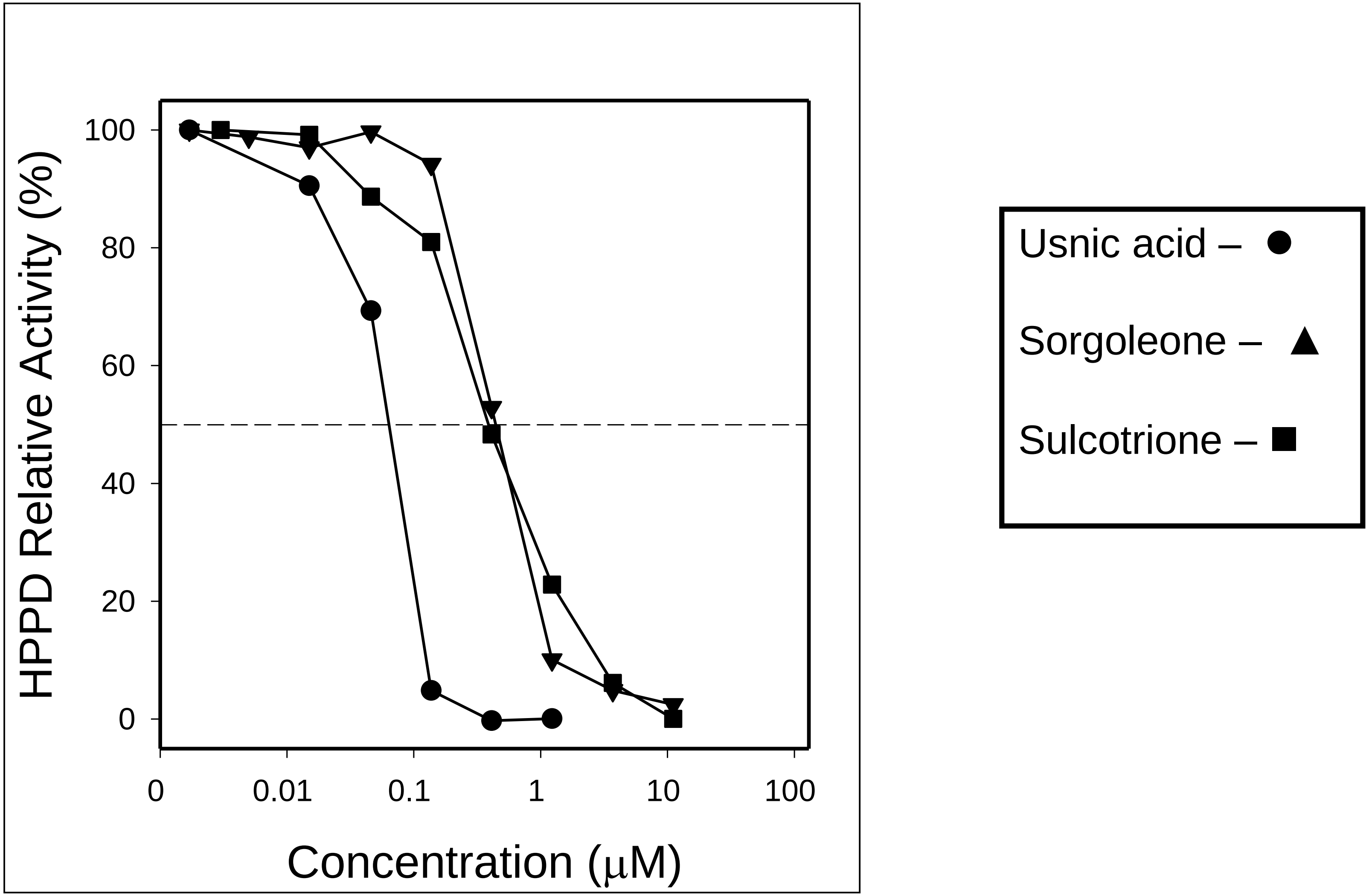
Leptospermone
from the bottlebrush plant



Sorgoleone from *Sorghum* spp.

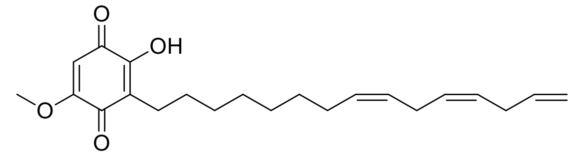



Tyrosine
TAT
4-hydroxyphenylpyruvate
HPPD
geranylgeranyl pyrophosphate
PSY
homogentisate
phytoene
PQ
PDS
PQH2
α-tocopherol
ζ-carotene
OH
O
sorgoleone
carotenoid

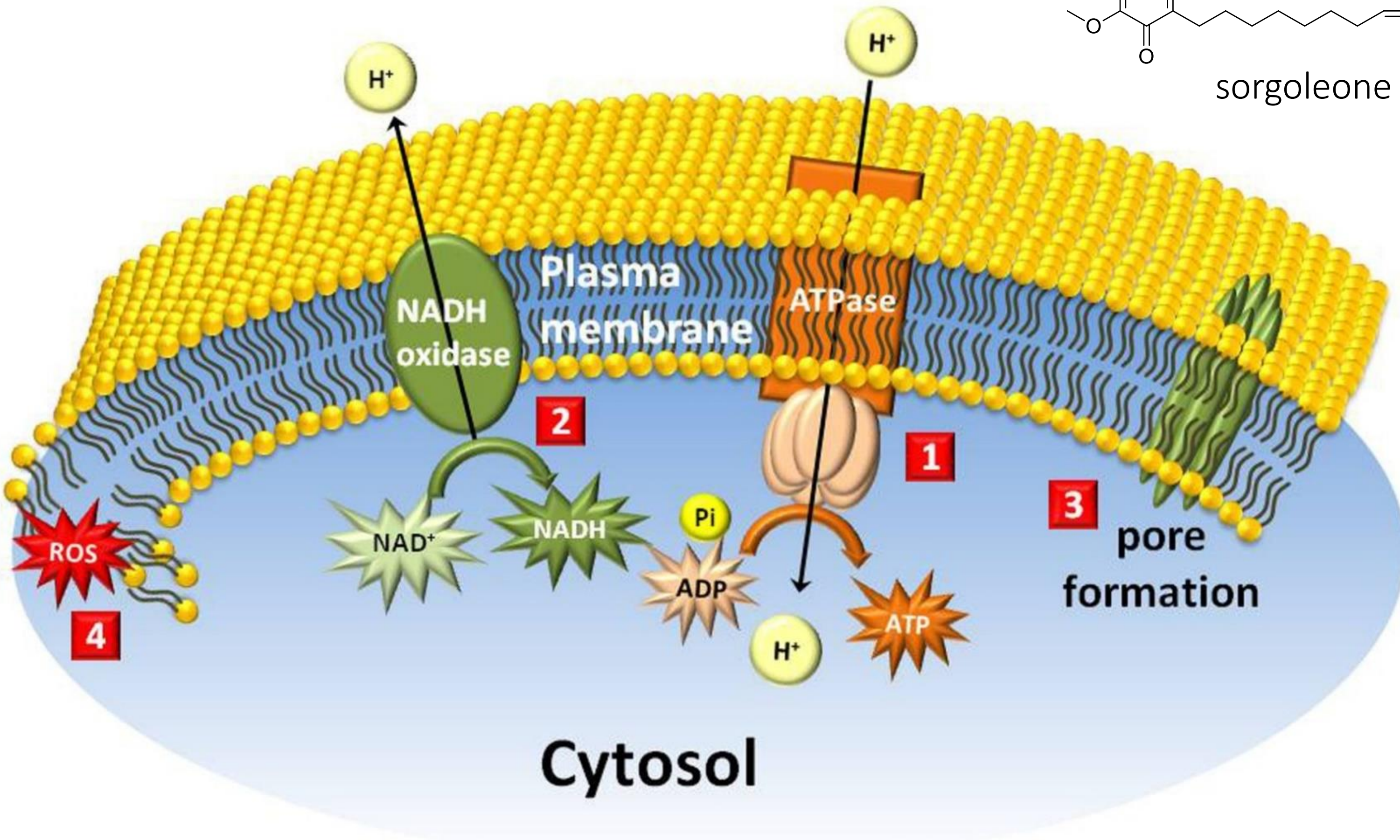

HPPD Relative Activity (%)
100
80
60
40
20
0
0
0.01
0.1
1
10
100
Concentration (µM)
Usnic acid –
Sorgoleone –
Sulcotrione –

USDA

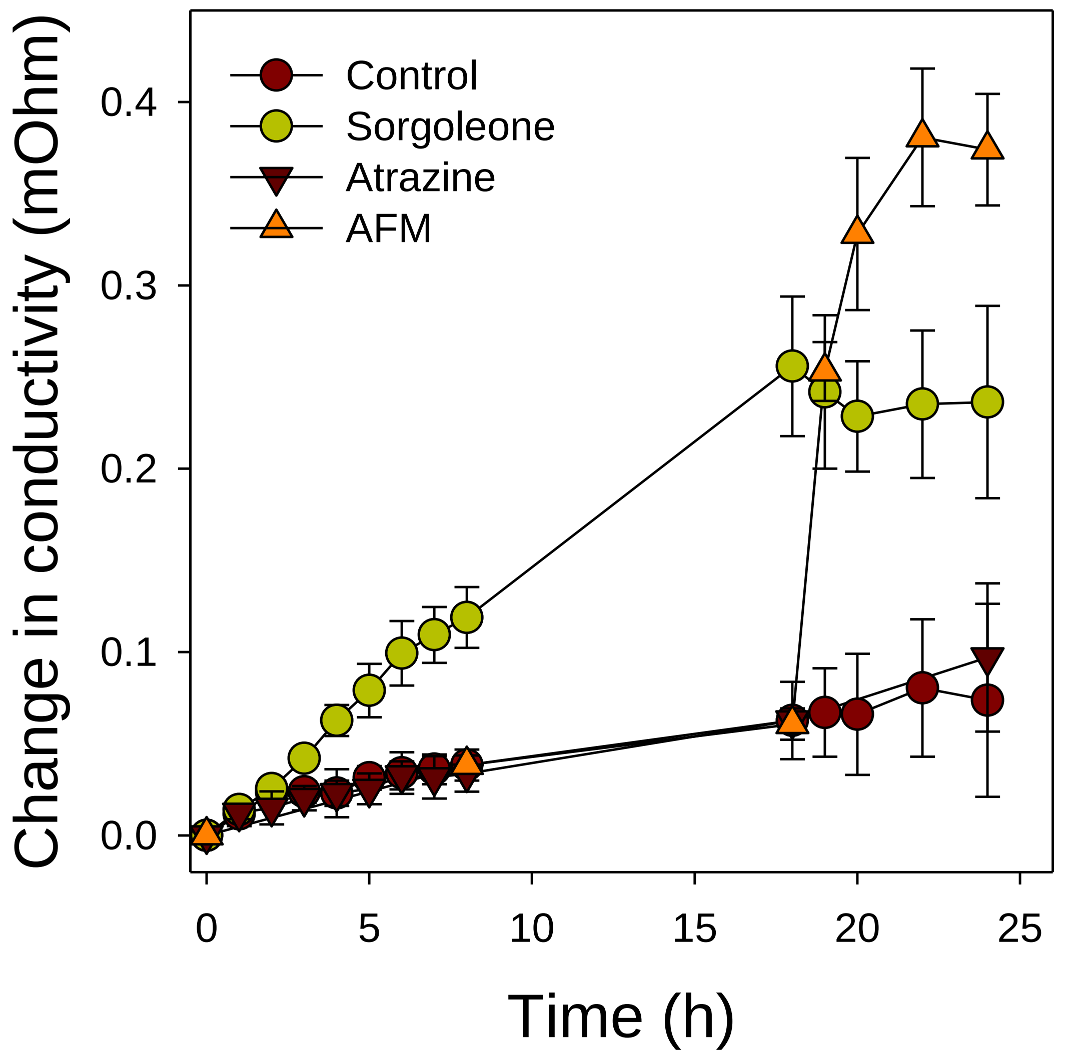
Hejl AM, Koster KL (2004) The allelochemical sorgoleone inhibits root H^+-ATPase and water uptake. Journal of Chemical Ecology 30:2181-2191



sorgoleone



Inhibition of root H^+-ATPase and water uptake


Control
Sorgoleone
Atrazine
AFM
Change in conductivity (mOhm)
0.0
0.1
0.2
0.3
0.4
0
5
10
15
20
25
Time (h)

frontiers in Plant Science

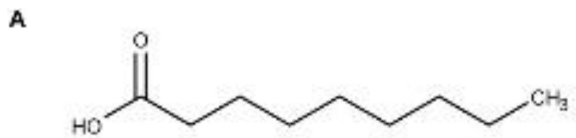
USDA

Front Plant Sci. 2019; 10: 329.
Published online 2019 Mar 18. doi: 10.3389/fpls.2019.00329

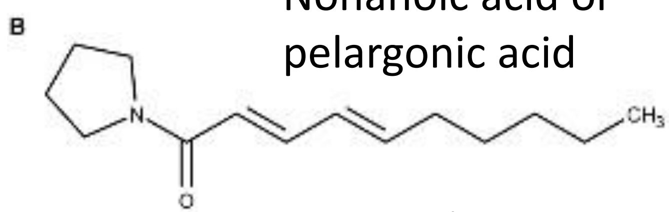
PMCID: PMC6431664
PMID: 30936889

Interactions Between Natural Herbicides and Lipid Bilayers Mimicking the Plant Plasma Membrane

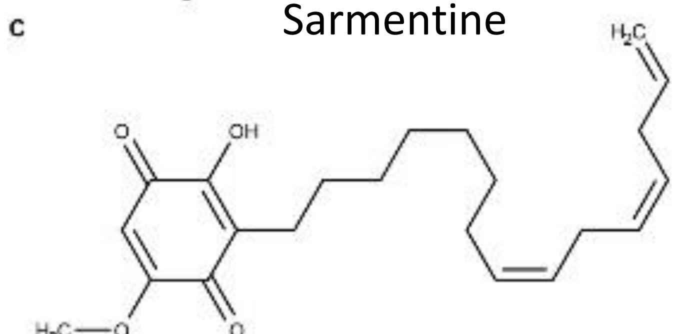
Simon Lebecque,[1,2] Laurence Lins,[1] Franck E. Dayan,[3] Marie-Laure Fauconnier,[4,†] and Magali Deleu[1,*†]



Nonanoic acid or pelargonic acid



Sarmentine



Sorgoleone

Sorgoleone was the only compound that:

1. had a clear effect on lipid fluidity in membranes

2. had a strong affinity for lipid bilayers

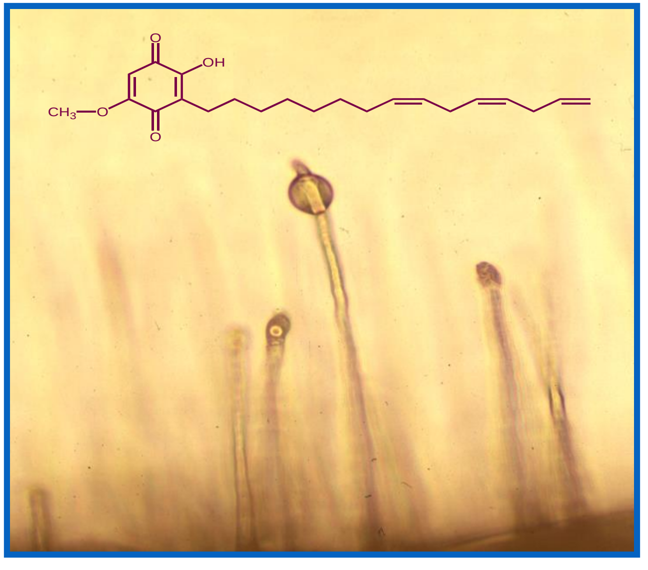
3. had a rigidifying effect on lipid bilayers

Advantages of manipulating sorgoleone production for weed management

- Only produced by root hairs, so metabolic cost of synthesis to the entire plant is low
- Multiple modes of action
- Relatively long soil half life

USDA

Probing the Sorgoleone Biosynthetic Pathways Using Expressed Sequence Tags



- Generate cDNA libraries for cell type where pathway is localized
  - root hairs (*Sorghum bicolor*)

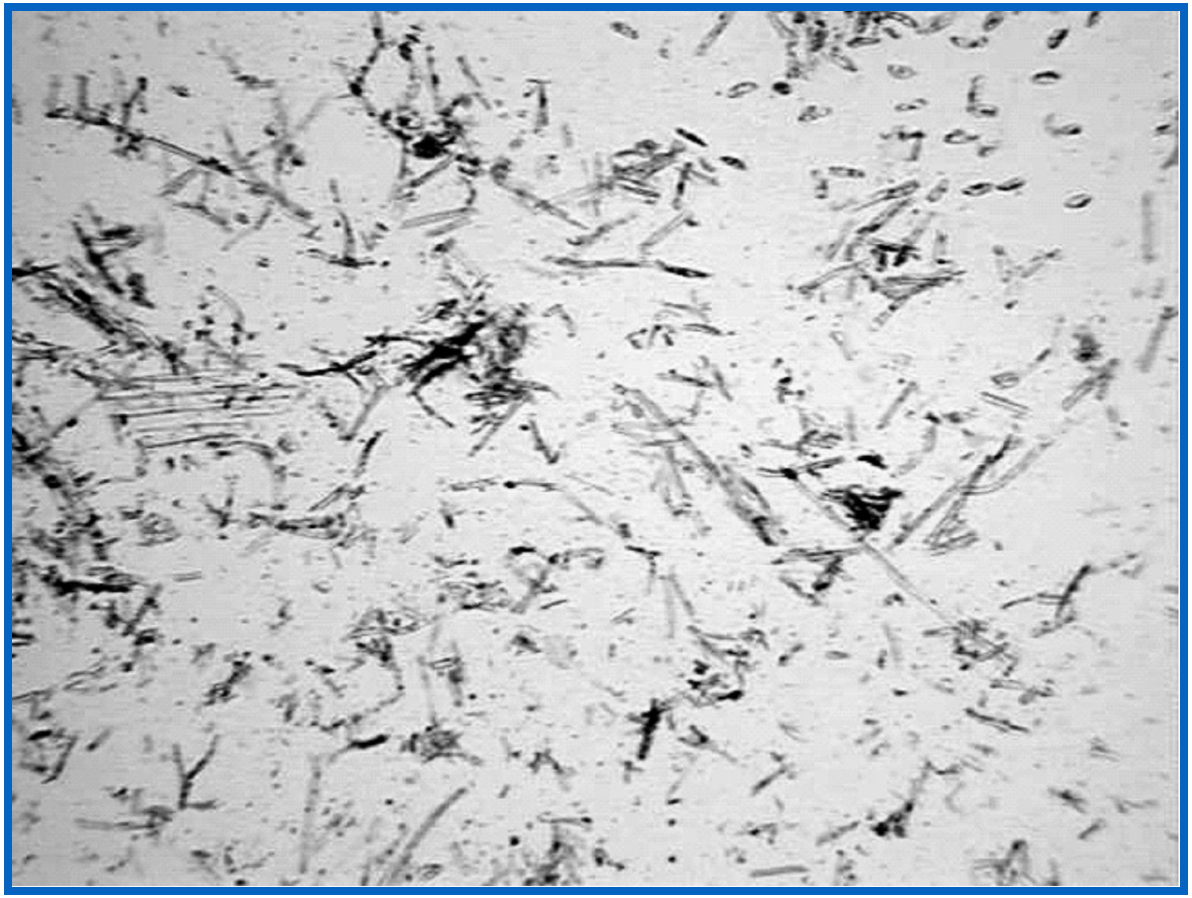
- EST sequencing (ca. 6,000 - 5' reads per library)

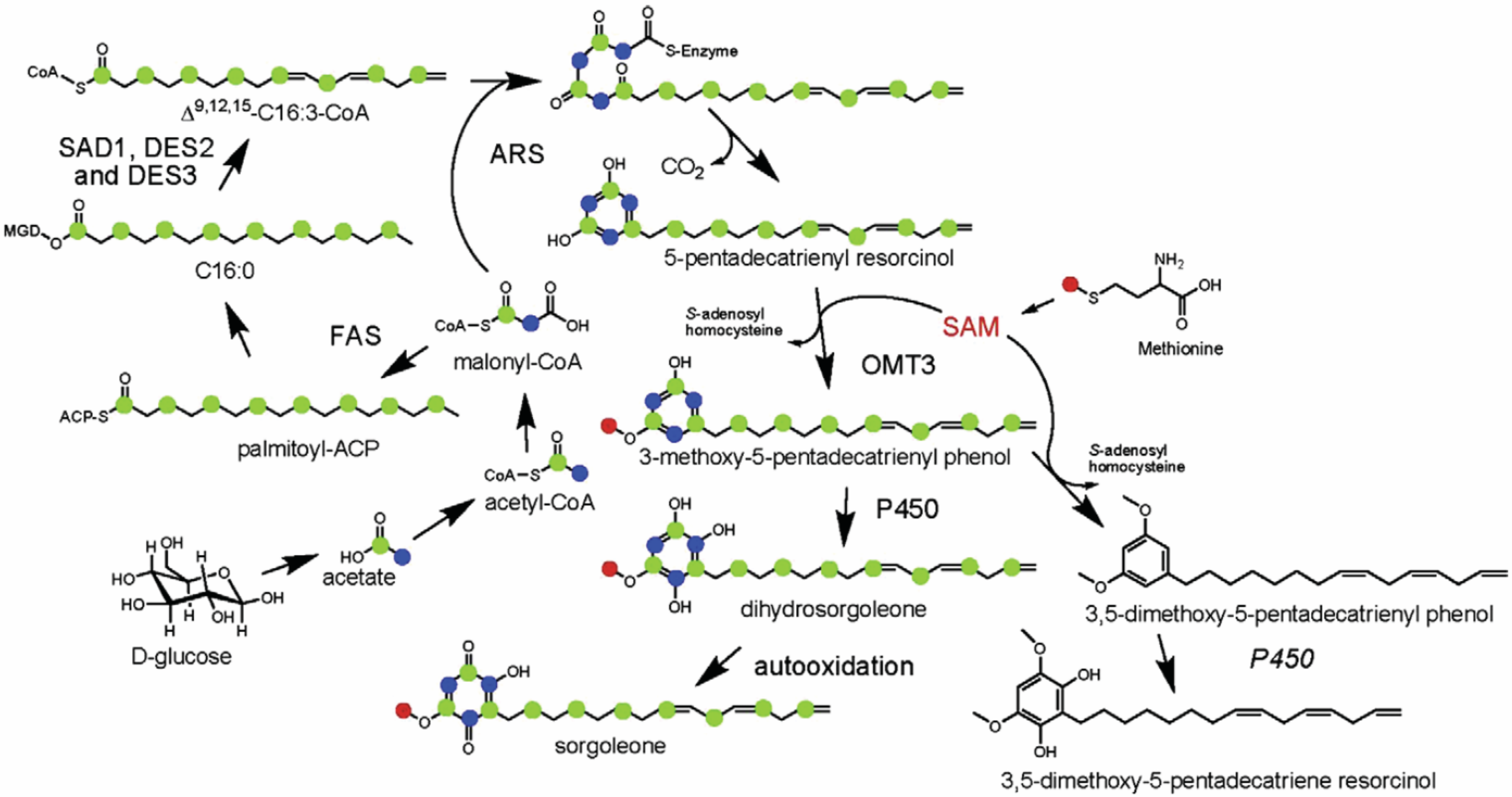
- Mine sequence data for highly expressed protein families related to pathway

- Functional characterization in heterologous system (e.g., *E. coli* or yeast)

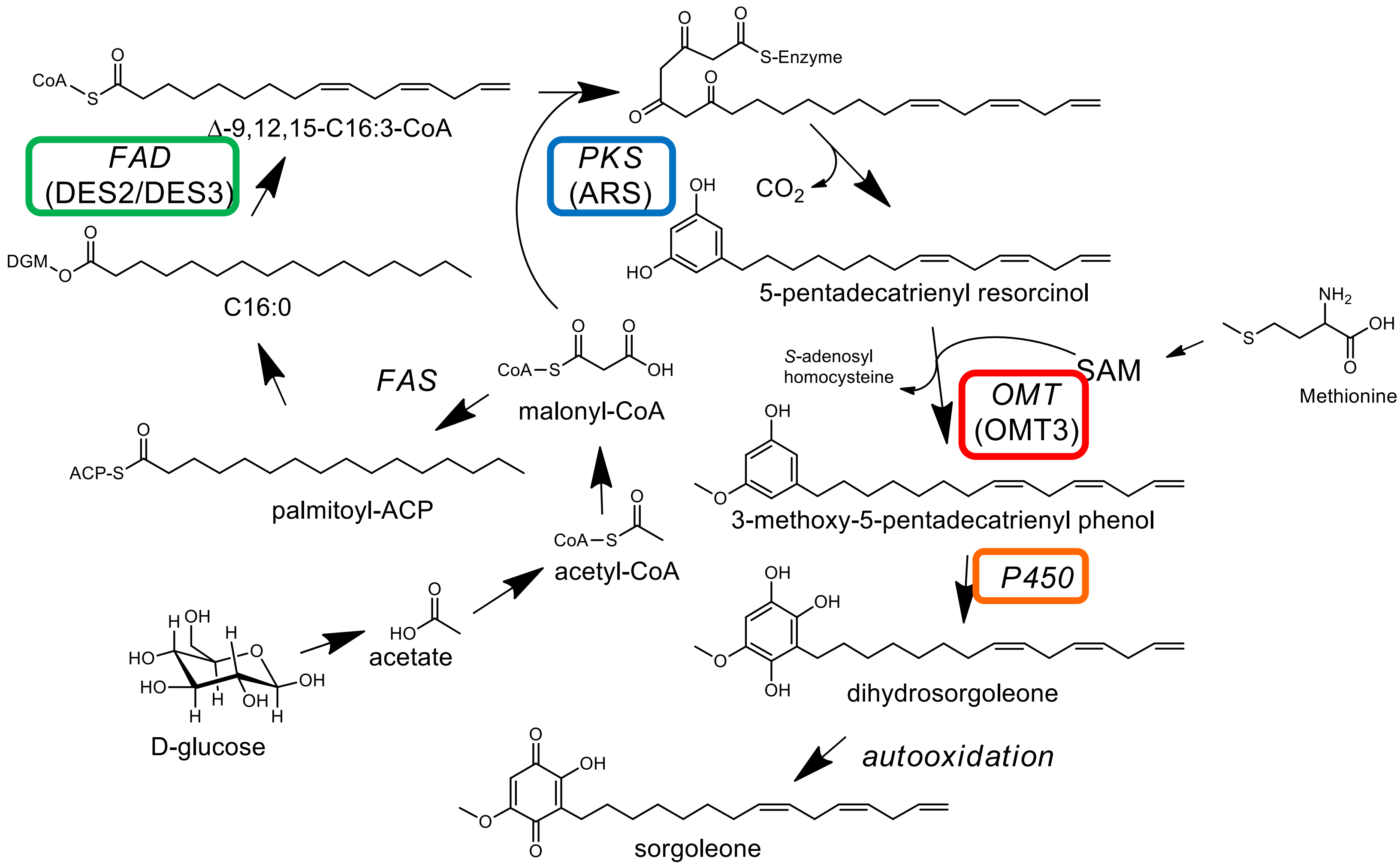
- *In vivo* confirmation of function via knockout or overexpression

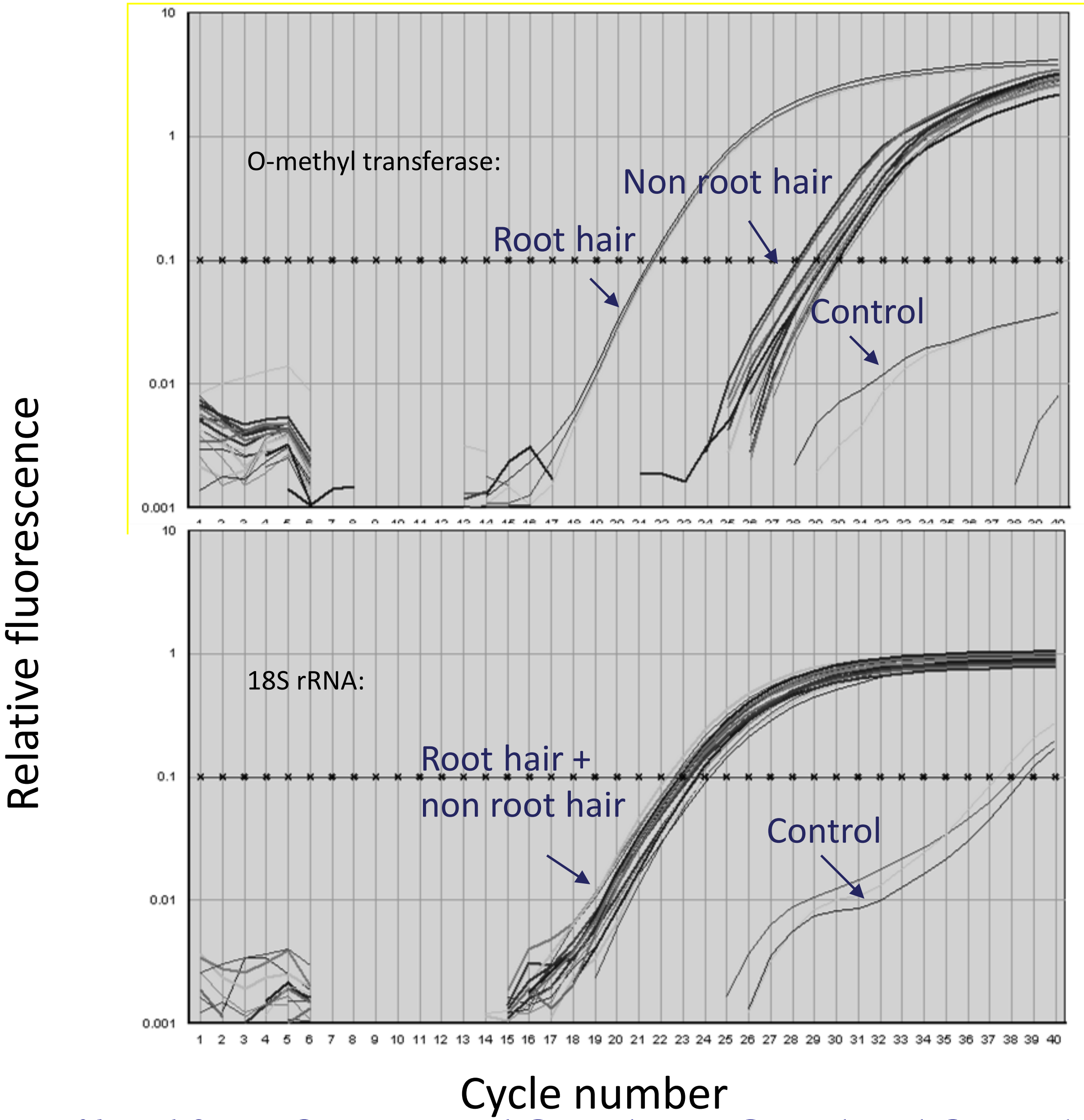
Isolated *Sorghum bicolor* root hairs



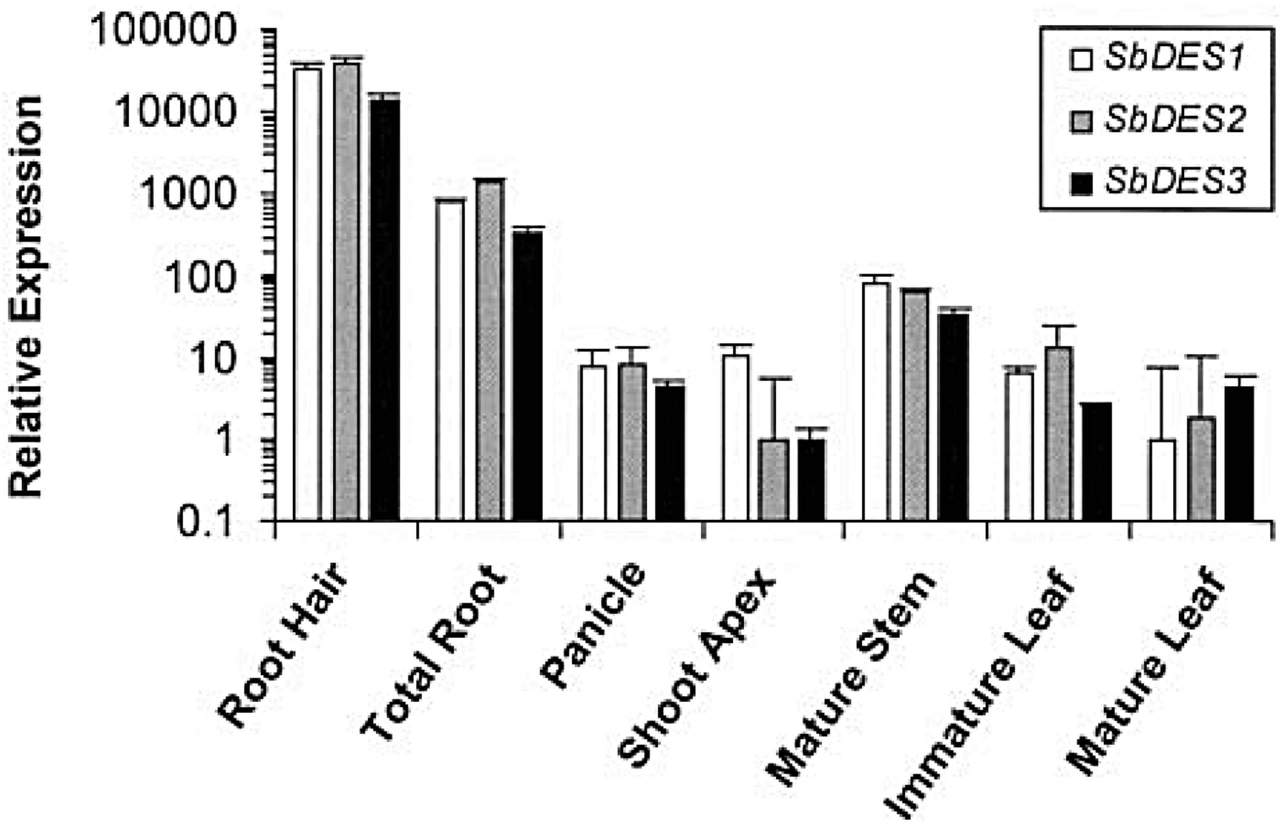


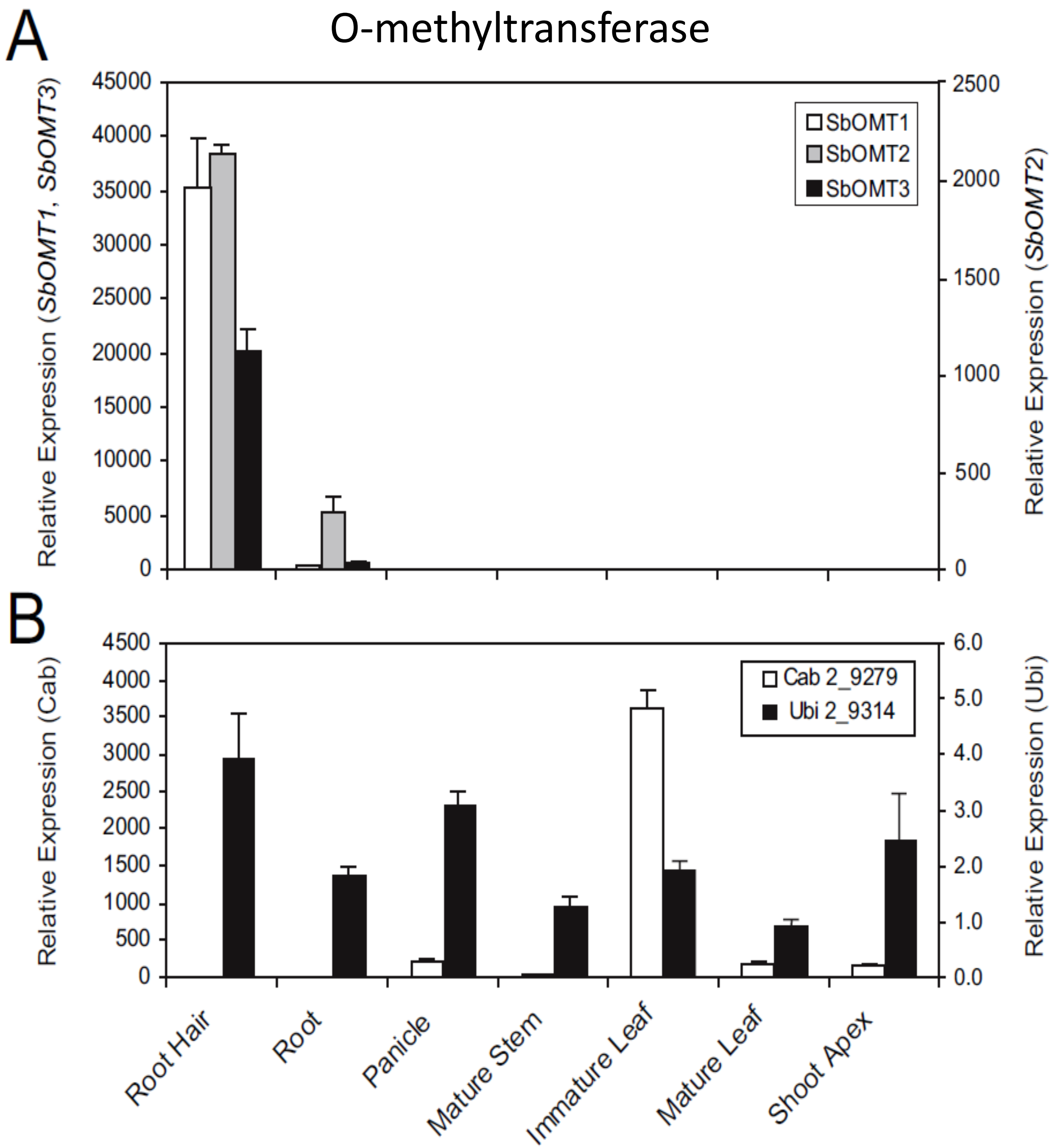
Dayan et al. (2003) *J. Biol. Chem*. 278:28607-28611.


CoA
S
O
Δ-9,12,15-C16:3-CoA
FAD
(DES2/DES3)
DGM
O
C16:0
PKS
(ARS)
S-Enzyme
CO2
OH
HO
5-pentadecatrienyl resorcinol
FAS
CoA–S
OH
malonyl-CoA
ACP-S
palmitoyl-ACP
S-adenosyl
homocysteine
SAM
NH2
Methionine
OMT
(OMT3)
3-methoxy-5-pentadecatrienyl phenol
acetyl-CoA
P450
HO
acetate
dihydrosorgoleone
D-glucose
H
autooxidation
sorgoleone

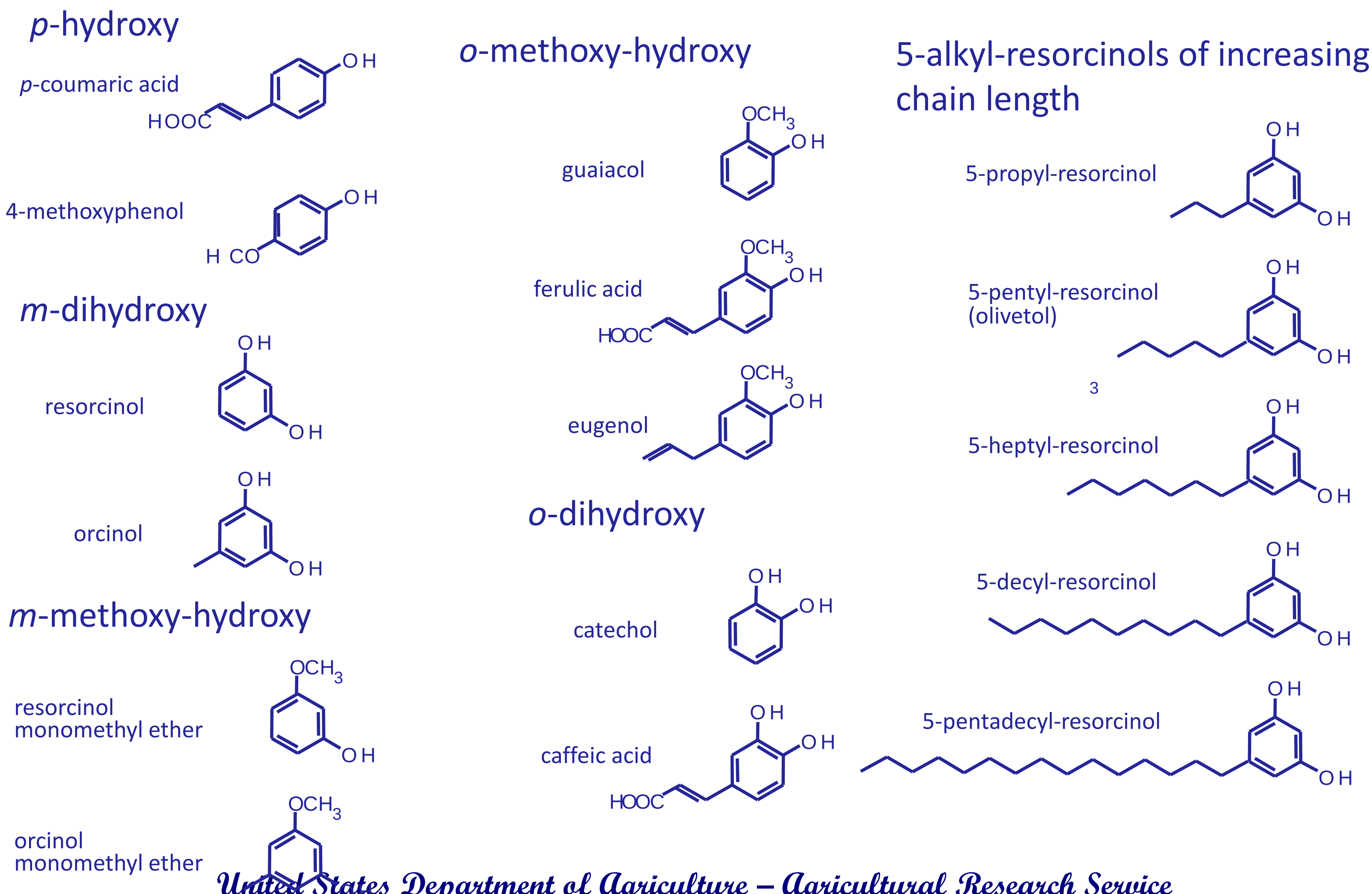

O-methyl transferase:
Root hair
Non root hair
Control
18S rRNA:
Root hair +
non root hair
Control
Relative fluorescence
Cycle number
10
1
0.1
0.01
0.001

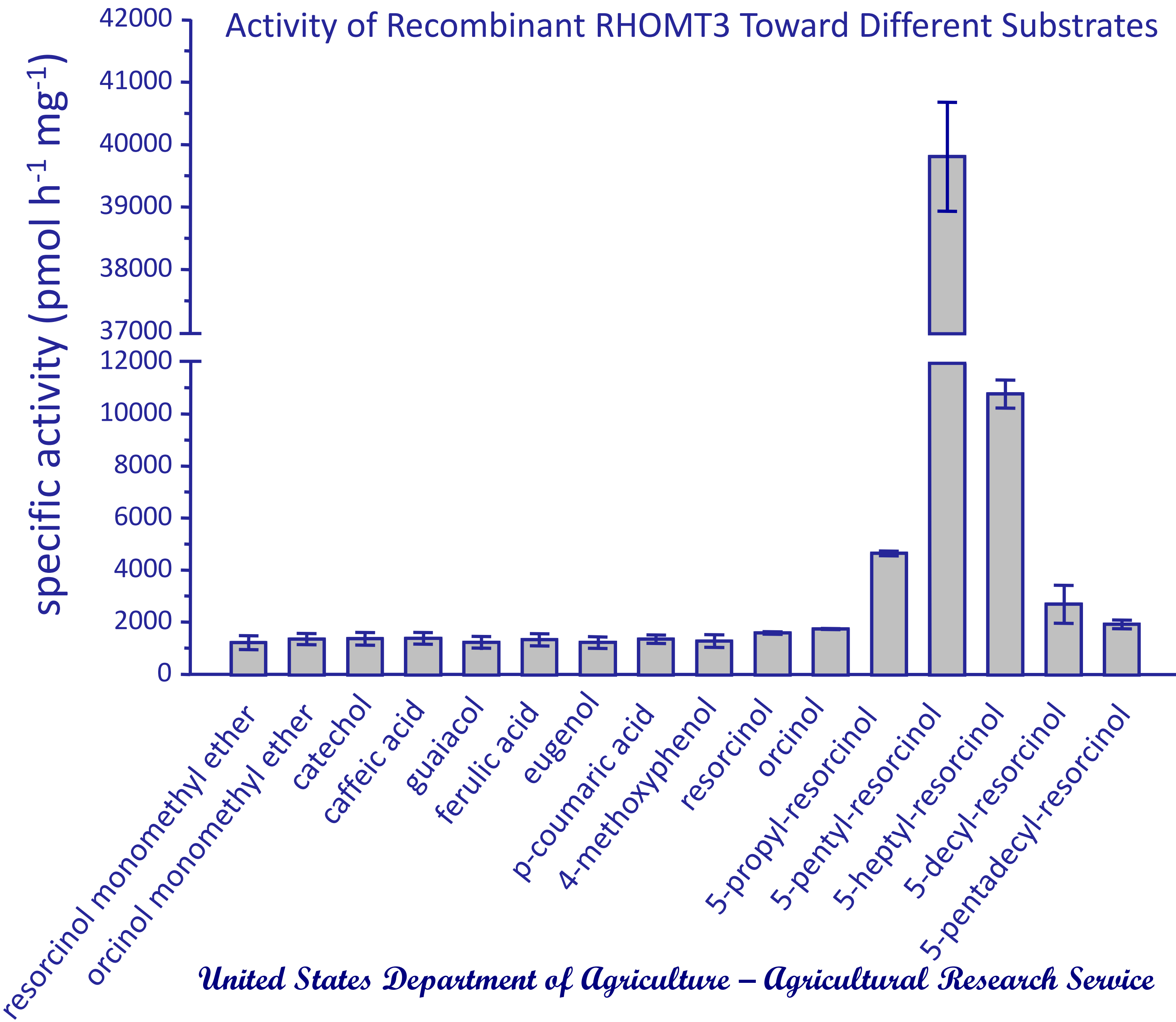
Fatty acid desturases



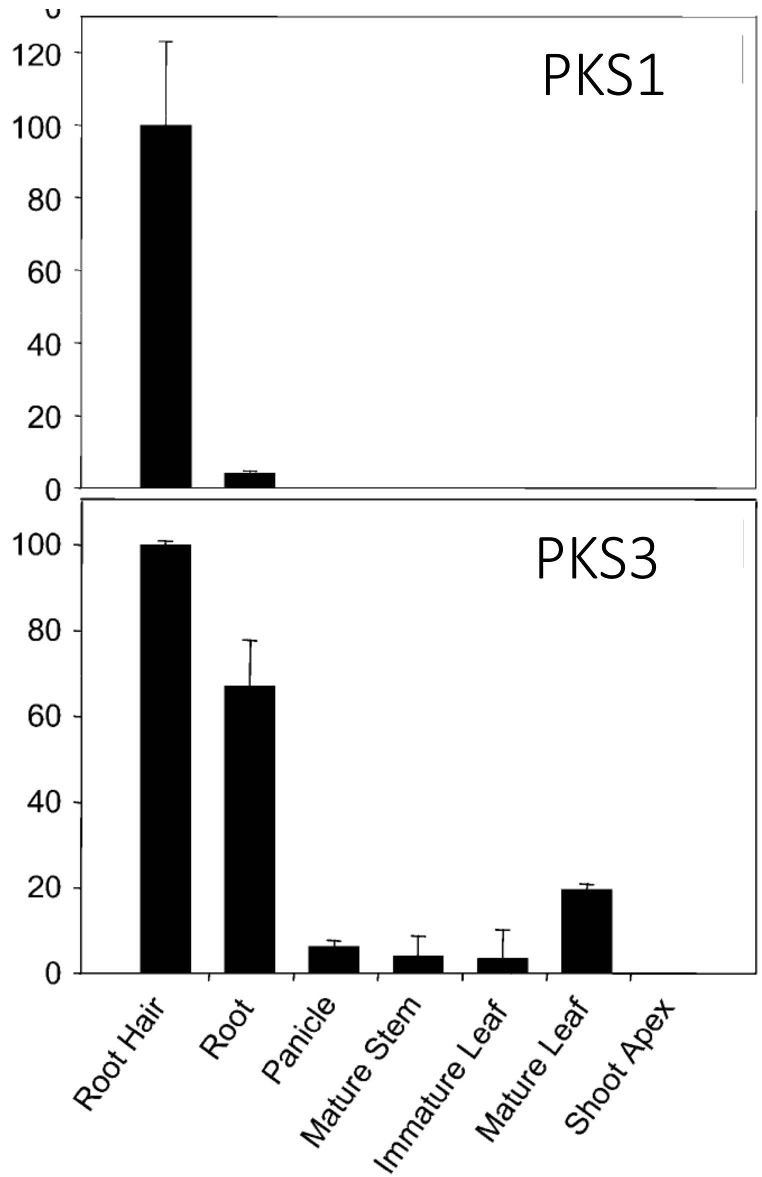

A
O-methyltransferase
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Relative Expression (SbOMT1, SbOMT3)
2500
2000
1500
1000
500
0
Relative Expression (SbOMT2)
SbOMT1
SbOMT2
SbOMT3
B
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Relative Expression (Cab)
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Relative Expression (Ubi)
Cab 2_9279
Ubi 2_9314
Root Hair
Root
Panicle
Mature Stem
Immature Leaf
Mature Leaf
Shoot Apex

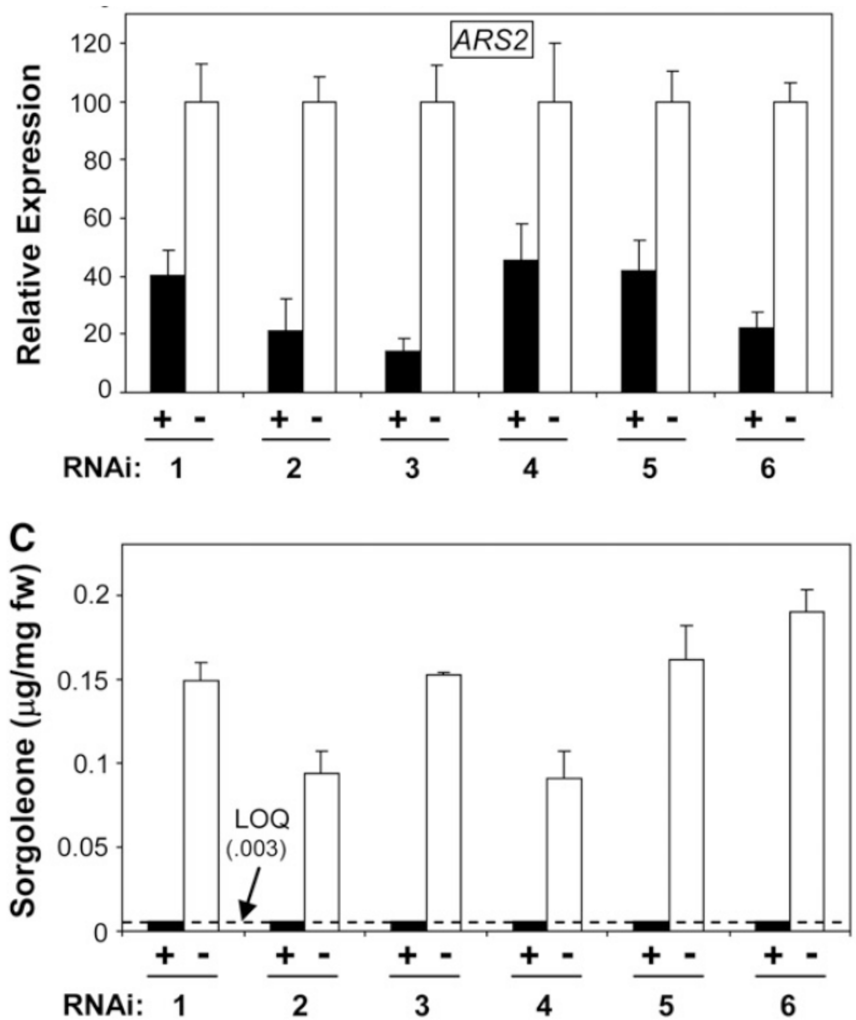
Substrates Tested With Recombinant *S. bicolor O*-Methyltransferases

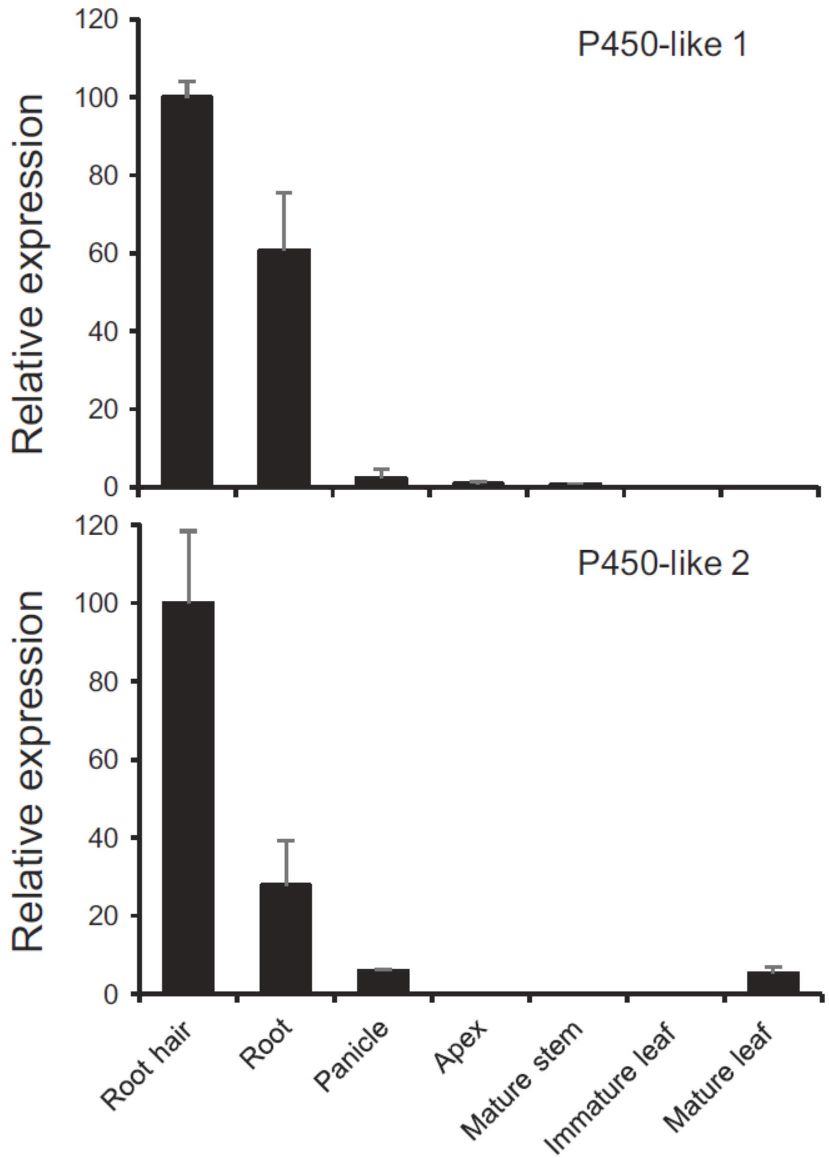



Activity of Recombinant RHOMT3 Toward Different Substrates
specific activity (pmol h-1 mg-1)
42000
41000
40000
39000
38000
37000
12000
10000
8000
6000
4000
2000
0
resorcinol monomethyl ether
orcinol monomethyl ether
catechol
caffeic acid
guaiacol
ferulic acid
eugenol
p-coumaric acid
4-methoxyphenol
resorcinol
orcinol
5-propyl-resorcinol
5-pentyl-resorcinol
5-heptyl-resorcinol
5-decyl-resorcinol
5-pentadecyl-resorcinol

Polyketide synthase




ARS2
Relative Expression
120
100
80
60
40
20
0
+ -
RNAi: 1 2 3 4 5 6
C
Sorgoleone (µg/mg fw)
0.2
0.15
0.1
0.05
0
LOQ
(.003)
+ -
RNAi: 1 2 3 4 5 6

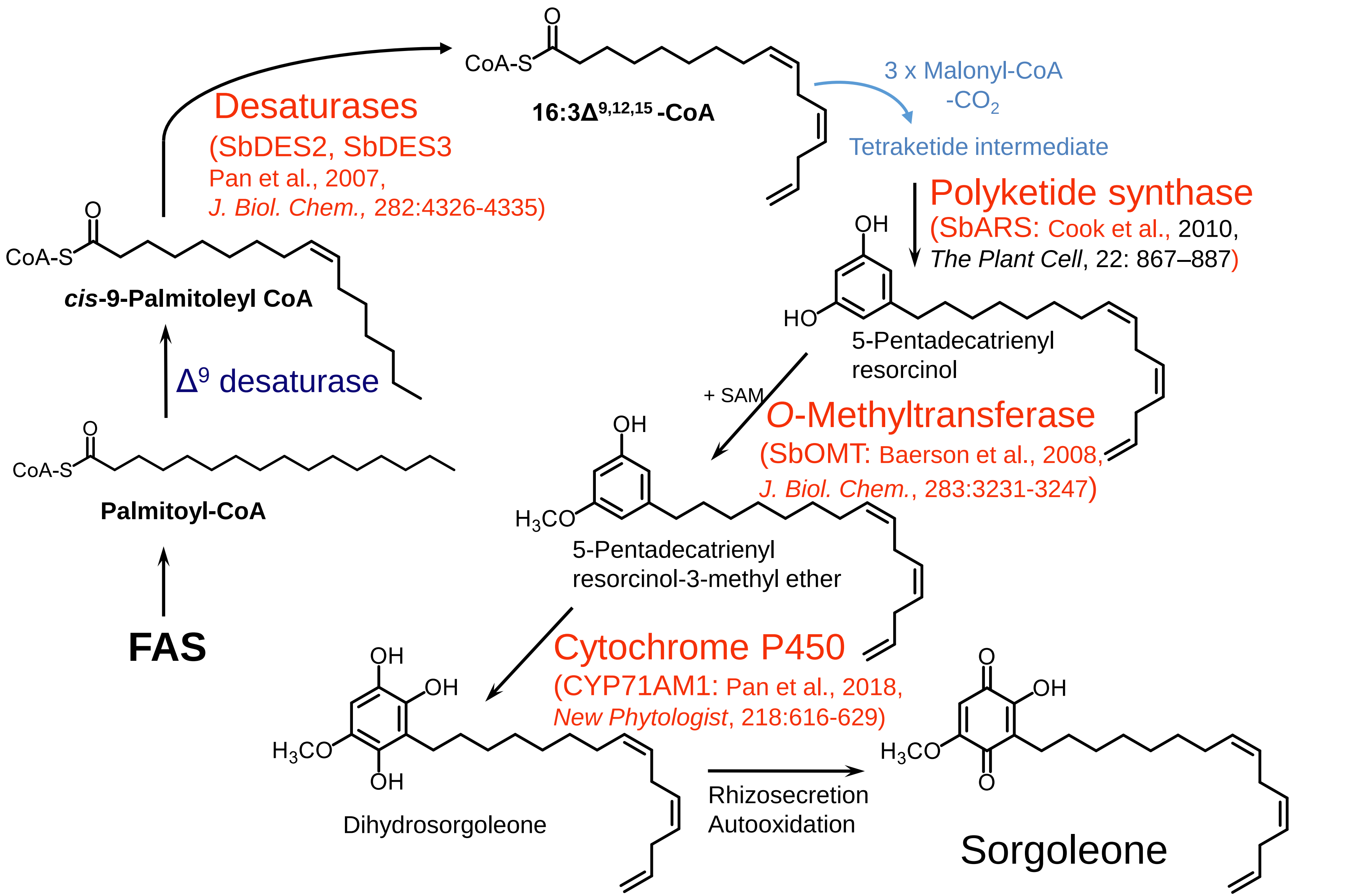


Pan et al.

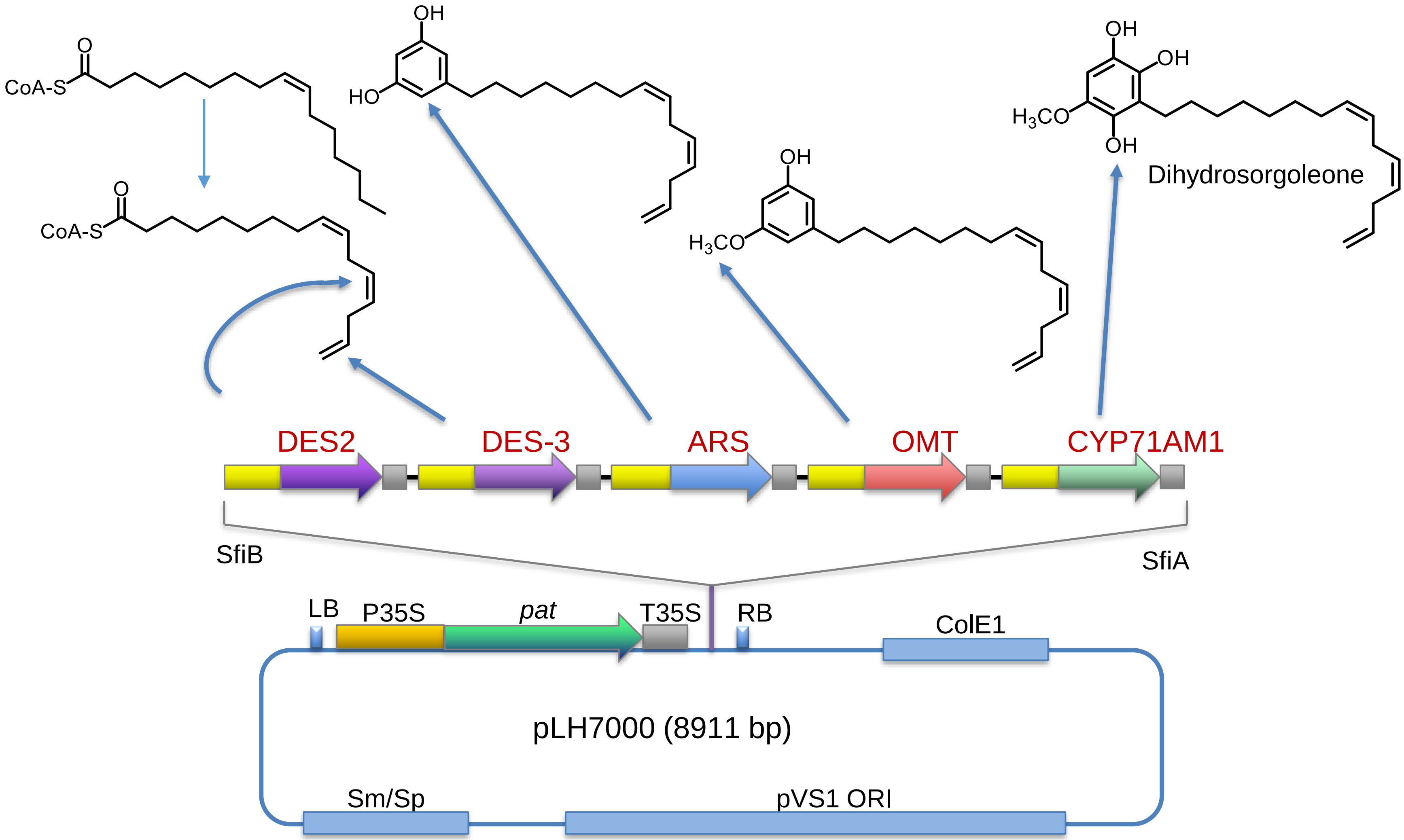
New Phytologist (2018) **218:** 616–629
doi: 10.1111/nph.15037

Sorgoleone biosynthetic pathway - Identify, isolate and functionally characterize genes/enzymes involved in sorgoleone biosynthesis

USDA



Construct for gene expression of entire sorgoleone biosynthetic pathway

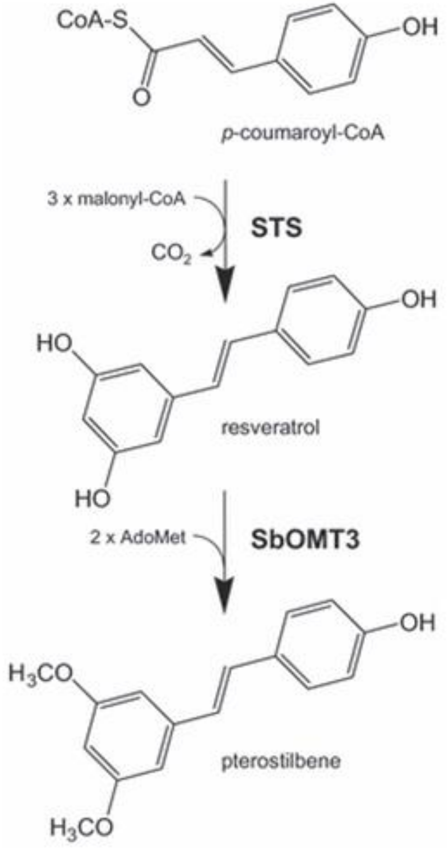


Rimando patents relating to sorgoleone

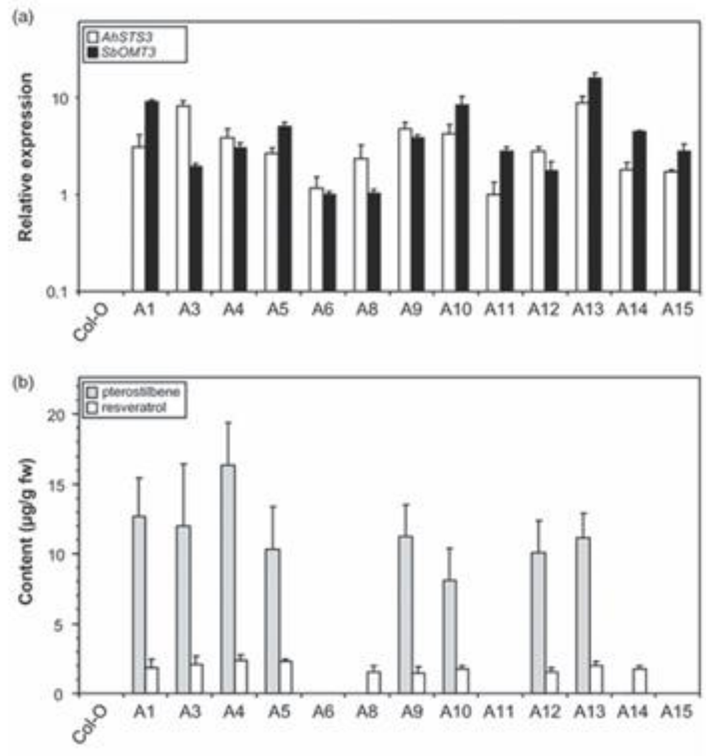
- Pan, Z., Rimando, A.M., Baerson, S.R. Genes encoding fatty acid Δ12- and Δ15-desaturases fro Sorghum bicolor. US Pat. (2013) US8383890 Ba 20130226.
- Baerson, S.R., Pan, Z., Rimando, A.M., Dayan, F.E., Cook, D. Two alkylresorcinol synthase genes from sorghum; cloning, expression, transformation and characterization. (February 2, 2016) US Patent 9,248, 145B2.
- Baerson, S.R., Rimando, A.M., Dayan, F.E., Pan, Z., Polachock, J.J. Methods for cloning Soghum root hair-specific OMT3 gene encoding O-methyltransferase and its use in pterostilbene and sorgoleone biosythesis in transgenic plants. US (2010) US 7732666 B1 20100608.

Spinoff

In planta **production of the highly potent resveratrol analogue pterostilbene via stilbene synthase and** ***O*****-methyltransferase co-expression**



In planta production of the highly potent resveratrol analogue pterostilbene via stilbene synthase and *O*-methyltransferase co-expression



Plant Biotechnology Journal
Volume 10, Issue 3, pages 269-283, 8 SEP 2011 DOI: 10.1111/j.1467-7652.2011.00657.x
http://onlinelibrary.wiley.com/doi/10.1111/j.1467-7652.2011.00657.x/full#f8

With co-authors, Agnes Rimando published more than a dozen papers and three patents on sorgoleone, a quinone produced by *Sorghum* spp. She was involved in showing that this compound is produced only in the root hairs of *Sorghum* spp. and that it is a good inhibitor of photosystem II of photosynthesis. It is used by the producing plant as an allelochemical to inhibit competing weeds. Her chemistry was instrumental in verifying the sorgoleone biochemical pathway and identifying the genes encoding the enzymes of that pathway. Some of this work was useful in her work on pterostilbene. Work with the sorgoleone pathway is leading to transgenically imparting sorgoleone production into other crops to enhance their weed-fighting capabilities.

ACS, August 27, 2019

EARLY CAREER DISCOVERY OF BIOACTIVE NATURAL PRODUCTS BY AGNES RIMANDO

MICHAEL APPELL
MYCOTOXIN PREVENTION AND APPLIED MICROBIOLOGY RESEARCH
UNITED STATES DEPARTMENT OF AGRICULTURE, AGRICULTURAL UTILIZATION RESEARCH
NATIONAL CENTER FOR AGRICULTURAL UTILIZATIONS RESEARCH
1815 N. UNIVERSITY ST. PEORIA, IL 61604 USA

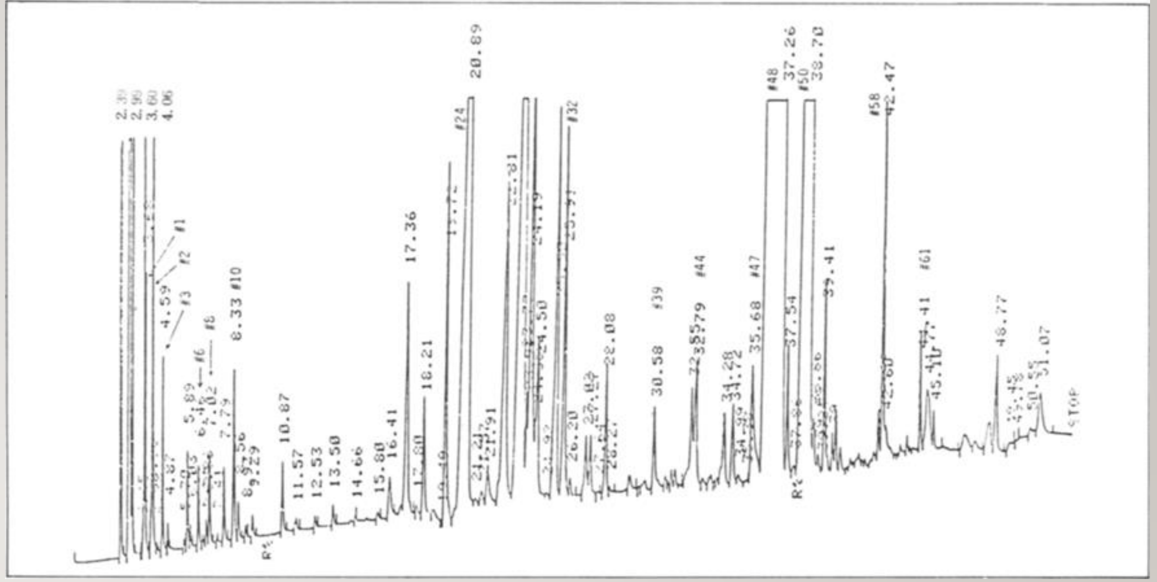
THE UNIVERSITY OF ILLINOIS AT CHICAGO
1859
COLLEGE OF PHARMACY

UIC COLLEGE OF PHARMACY – DEPARTMENT OF MEDICINAL CHEMISTRY & PHARMACOGNOSY

- Pharmacognosy - the branch of knowledge concerned with medicinal drugs obtained from plants or other natural sources.
- Natural Product Bioactivities and Isolation
- New Plant and Natural Product Discovery

Studies on the Constituents of Philippine *Piper betle* Leaves

Agnes M. Rimando*, Byung Hoon Han,
Jeong Hill Park and Magdalena C. Cantoria*
Natural Products Research Institute, Seoul National University, Seoul 110, Korea



Essential Oils

- 14 volatile compounds identified from Phillippine Piper betle Leaves
- 8 allypyrocatechol analogs were isolated and identified from the essential oil and ether fractions of Philippine Piper betle leaves (Piperaceae).
- Oil containted chavlbetol and chavlbetol
- The major component of the ether soluble fraction was aflylpyrocatechol

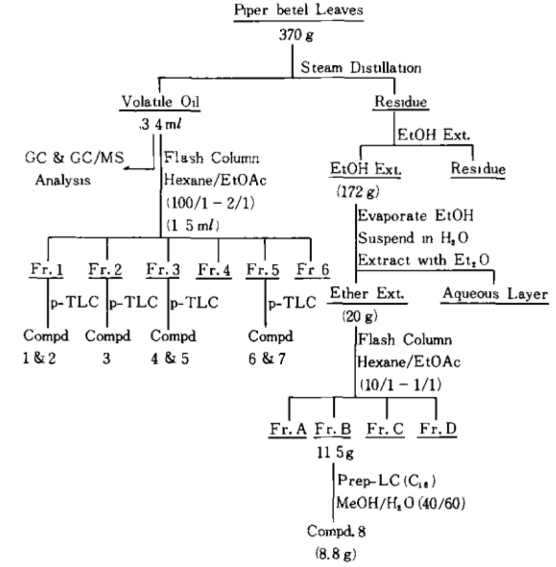


Fig. 1. Scheme for the Isolation of the Constituents of the Leaves of *Piper betle* Linne (Piperaceae).

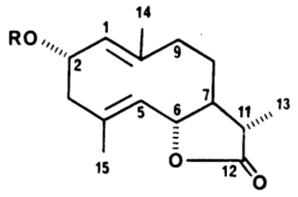
Table I. Identified Constituents of *Piper betle*

Peak No.*	Retention time	Compound Name	Formula	MW	Content** (%)
1	3 68	*alpha*-Pinene	$C_{10}H_{16}$	136	0 21
2	4. 06	Camphene	$C_{10}H_{16}$	136	0. 48
3	4. 59	*beta*-Pinene	$C_{10}H_{16}$	136	0 21
6	6 46	*d*-Limonene	$C_{10}H_{16}$	136	0 13
8	7 02	1, 8-Cineole	$C_{10}H_{18}O$	154	0. 03
10	8 33	*para*-Cymene	$C_{10}H_{14}$	134	0 08
24	20 89	Caryophyllene	$C_{15}H_{24}$	204	3 79
39	30. 58	Safrole	$C_{10}H_{10}O_2$	162	0. 11
44	32 79	Methyl chavibetol	$C_{10}H_{14}O_2$	178	0 72
47	35 68	Eugenol	$C_{10}H_{12}O_2$	164	0 42
48	37 26	Chavibetol	$C_{10}H_{12}O_2$	164	53 10
50	38. 70	Chavibetol acetate	$C_{12}H_{14}O_3$	206	15. 50
58	42. 47	Allylpyrocatechol diacetate	$C_{13}H_{14}O_4$	234	0 61
61	44 41	Allypyrocatechol monoacetate	$C_{11}H_{12}O_3$	192	
		Allylpyrocatechol	$C_9H_{10}O_2$	150	2 38***

Arch. Pha~. Res 9(2), 93--97 (1986)

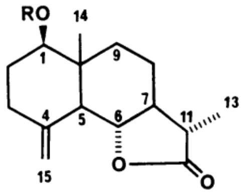
Sesquiterpene Lactones and Other Constituents from a Cytotoxic Extract of *Michelia floribunda*[1]

Ing-On Mondranondra,[2,3] Chun-tao Che,[2,4] Agnes M. Rimando,[2] Srunya Vajrodaya,[3] Harry H. S. Fong,[2] and Norman R. Farnsworth[2]



1 11β,13-Dihydrotamaulipin A β-D-glucoside
R = Glucose
3 11β,13-Dihydrotamaulipin A
R = H
4 Tamaulipin A
R = H, $\Delta^{11,13}$

Scheme I



2 11β,13-Dihydroreynosin β-D-glucoside
R = Glucose
5 11β,13-Dihydroreynosin
R = H

Scheme II

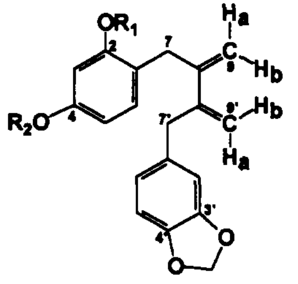
- Cytotoxic activity from the pentane and CHC13 fractions of a crude extract of *Michelia floribunda* in KB and P388 tumor cell cultures.
- Chromatographic isolation of three cytotoxic sesquiterpene lactones (costunolide, parthenolide, and santamarine) and a cytotoxic isoquinoline alkaloid (liriodenine).
- The structures of these new compounds were determined through interpretation of their spectroscopic data including 2D-NMR spectroscopy. Syringin was also isolated from the extract.
- Dihydro derivatives and isoloated syringin lacked cyctotoxicty

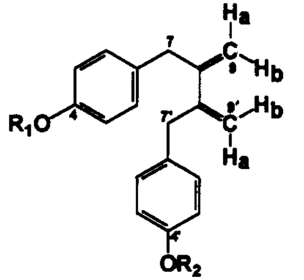
Pharmaceutical Research, Vol. 7, No. 12, 1990

NEW LIGNANS FROM *ANOGEISSUS ACUMINATA* WITH HIV-1 REVERSE TRANSCRIPTASE INHIBITORY ACTIVITY

AGNES M. RIMANDO, JOHN M. PEZZUTO, NORMAN R. FARNSWORTH,*

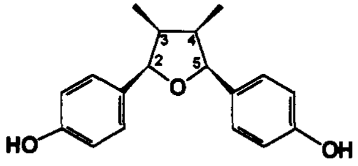
- New dibenzylbutadiene lignans were isolated from *Anogeissus acuminate*. Compounds 1 and 3 were identified as the active HTV-1 reverse transcriptase (RT) inhibitory constituents of this plant obtained by bioassay-guided fractionation.
- Synergistic effects of Compound 3, which was very weakly active when tested alone, showed high activity when combined with 1.
- The structures were established by spectroscopic methods, especially by ID and 2D nmr experiments





1 $R_1=R_2=H$
2 $R_1=R_2=CH_3$

3 $R_1=R_2=H$
4 $R_1=R_2=CH_3$



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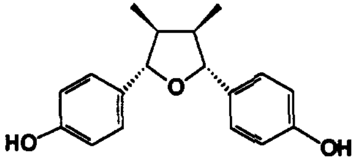

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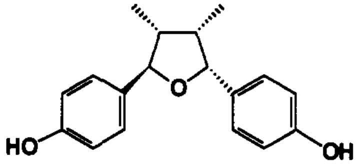

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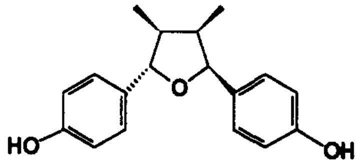

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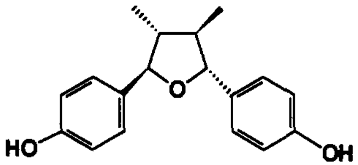

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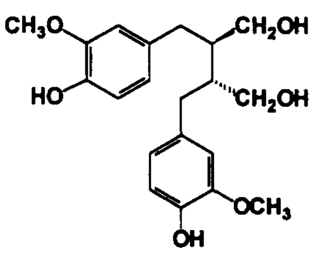

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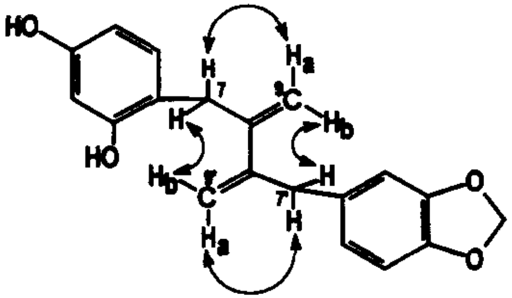


FIGURE 1. Significant NOe Correlations of **1**.

Journal of Natural Products
Vol. 57, No. 7, pp. 896-904, July 1994

Electrospray Liquid Chromatography/Mass Spectrometry of Ginsenosides

Anal. Chem. **1995**, *67*, 3985–3989

Richard B. van Breemen,* Chao-Ran Huang, Zhi-Zhen Lu, Agnes Rimando,† Harry H. S. Fong, and John F. Fitzloff

Department of Medicinal Chemistry and Pharmacognosy, University of Illinois at Chicago (m/c 781), 833 South Wood Street, Chicago, Illinois 60612-7231

LC/MS comparative study and method has been developed for the analysis of ginseng saponins (ginsenosides) contained in extracts of the root of ginseng (Korean ginseng) and quinquefolius (American ginseng).

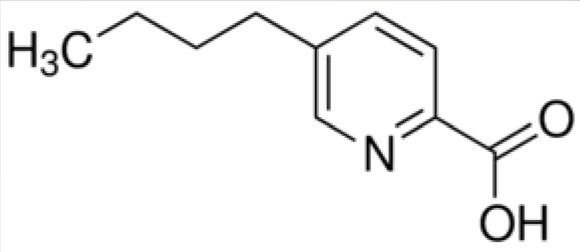
The LC/MS method consists of separation of ginsenosides using an (aminopropyl)silica HPLC column, followed by detection using a photodiode array UV absorbance detector and then on-line electrospray mass spectrometry.

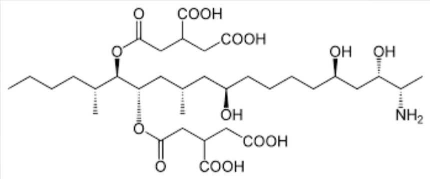
The first application of electrospray mass spectrometry and LC/MS to the analysis of ginsenosides is reported. Besides facilitatingthe identification of ginsenosidesin extracts of ginseng, electrospray LC/MS also provided a ginsenoside profile that distinguished one varietyof ginseng from another.

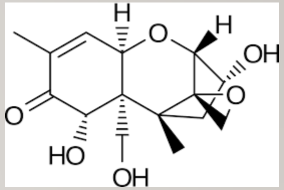
LACTATIONAL PASSAGE OF FUSARIC ACID FROM THE FEED OF NURSING DAMS TO THE NEONATE RAT AND EFFECTS ON PINEAL NEUROCHEMISTRY IN THE F1 AND F2 GENERATIONS AT WEANING

James K. Porter, Emma M. Wray, Agnes M. Rimando, Philip C. Stancel, Charles W. Bacon, Kenneth A. Voss

Toxicology and Mycotoxin Research Unit, R. B. Russell Agriculture Research Center, Athens, Georgia, USA







Journal of Toxicology and Environmental Health, 49:161-175, 1996

Fusaric acid (FA) is produced by several Fusarium species that commonly infect cereal grains and other agricultural commodities.

Mycotoxin Produced by *Fusarium* species and can be found in corn.

Discoverd that fusaric acid in feed ingested by pregnant rats is passed to the neonate via the milk (colostrum) at least within 4 d postpartum.

After parturition, the first 4-7 d are times most critical to the neonate.

During this period, decreased milk production with additional exposure to mycotoxins could be detrimental.

Although fusaric acid does not appear to have any adverse affects on the developing fetus and apparently is not acutely toxic to the adult or neonate rat prenatally exposed to the mycotoxin, there exists the potential for its synergistic effects with other mycotoxins (fumonisins and deoxynivalenol).

FUSARIC ACID INCREASES MELATONIN LEVELS
IN THE WEANLING RAT AND IN PINEAL CELL CULTURES

Agnes M. Rimando, James K. Porter
Richard B. Russell Agricultural Research Center, Toxicology and Mycotoxin Research Unit, Athens, Georgia, USA

Fusaric Acid in the feed of nursing rats is passed to the suckling offspring and alters serotonin (5-hydroxytryptamine, 5HT) in the neonate rat.

5HT is involved in melatonin (MEL) production by the pineal gland. MEL is a hormone important in reproduction and seasonality in animals.

At 200 ppm in the diet of nursing dams, FA increased serum MEL in both sexes. Results obtained from ELISA were supported by high-performance liquid chromatography (HPLC) analysis with fluorescence detection.

Division of Agricultural and Food Chemistry Leader

- AGFD Chair
- AGFD Councilor
- AGRO Liaison
- Spence Award Liaison
- AGFD Functional Foods & Natural Products Subdivision Chair
- Goals of AGFD Strategic Plan
- Local Section Chair, Section Chemist Award
- Distinguished Service Award, ACS Fellow, AGFD Fellow, Spencer Award
- Organizer of many symposia that attracted future division leaders

- Vision: Enhance quality of life by advocating safe, nutritious and sustainable food and agricultural supplies that meet global challenges.
- Mission: Lead and foster a diverse community to promote and advance agricultural and food chemistry research, education, outreach and communication

Agnes Rimando received the 2016 **Kenneth A. Spencer Award** for Outstanding Achievement in Agricultural and Food Chemistry. The award is given by the Kansas City Section of the ACS. The Spencer Award, the most prestigious ACS award recognizing advancements in agricultural and food chemistry is the latest of the numerous awards she has received for her work and patents on the chemistry and health benefits of blueberries and other natural food products. Agnes is a former chair of the AGFD division and a frequent contributor to and organizer of AGFD symposia.

Thank you

Agnes Rimando, Scientist and International Ambassador

H. N. Cheng
USDA Agricultural Research Service
Southern Regional Research Center
New Orleans, LA 70124, USA

August 27, 2019

Agnes Rimando, eminent scientist

- One of the most successful scientists at USDA (1994 – 2018).
- Widely respected for her expertise in the chemistry of plants.
  - Best known for her work on pterostilbene (from grapes and blueberries).
- Published about 200 papers, served as invited speaker at numerous symposia.
- Recognized by USDA:
  - Technology Transfer Award
  - Mid-South Area Technology Award
  - Mid-South Area Senior Scientist Award
- Recognized outside of USDA:
  - Kenneth Spencer Award
  - ACS Ole Miss Section Scientist Award
  - ACS Fellow and AGFD Fellow

Agnes Rimando, International scientist

- Born and grew up in the Philippines.
- Received B.S. and M.S. degrees from the Univ. of Philippines.
- Served as UNESCO Scholar in Korea in 1985
- Worked at Hiroshima University (Japan) School of Medicine in 1985-1987
- Received her doctorate at the Univ. of Illinois at Chicago in 1993
- After joining USDA in 1994, she interacted and collaborated with many scientists overseas.
- Served as a consultant all over the world for the USDA and the US State Department, including travels to Denmark, Rwanda, Colombia.

Agnes Rimando, ACS leader

- Chair, Ole Miss Section, 2008-09
- AGFD Division, Chair, 2007, Chair-Elect, 2006, Alt. Councilor, 2002-2004; Councilor, 2010-18
- Committee on Analytical Reagents, Associate, 2004-05
- Committee on International Activities (IAC), Associate, 2011-12; Member, 2013-18.
- Chair of IAC Subcommittee on Asia Pacific, 2014-18.
- (Non-ACS) President of the American Council for Medicinally Active Plants; member of Amer. Soc. of Pharmacognosy and Int'l Allelopathy Society

Agnes Rimando, Int’l Ambassador

- Chair of IAC Subcommittee on Asia Pacific, 2014 - 2018
- Convened the subcommittee meetings at ACS National Meetings
- Hosted Asia Pacific visitors and discussed possible joint activities and programs
- Reviewed applications for new international chapters from the Asia Pacific region
- Encouraged and participated in joint activities relating to the Asian Pacific international chapters
- Organized symposia and edited books involving Asian Pacific scientists

ACS International Activities Committee, 2018

Several Examples

Agnes Rimando,
Int'l Ambassador

Agnes did a lot to advance the global chemistry enterprise. The following examples show only a sampling of her contributions, and they reflect the breadth of her reach and the depth of her talent

- *First Joint ICSCT-AGFD Symposium, 2014*
- *International Entrepreneurship Symposium, 2015*
- *BOOST workshops in Thailand, 2015*
- *AGFD Symposium on "Chemistry of Korean Foods and Beverages", 2017*
- *Asia Pacific International Chapters Conference, 2017*

First Joint ICSCT-AGFD Symposium, 2014

- This was the first international scientific meeting jointly organized by an ACS international chapter (Thailand) and an ACS Division (AGFD) in Bangkok on March 4-5, 2014.
- The main organizers were Agnes Rimando and Kanjana Matattanatawee (Siam Univ.), with help from others
- The symposium consisted of four topics, viz., food bioactives & health, flavor chemistry, food safety, and dairy products.
- 180 speakers from 12 countries participated, including university, industry, and government scientists, and students from 25 universities.
- Included in the program was a popular poster competition for graduate students.
- This event won the P3 Award given by ACS in 2014.

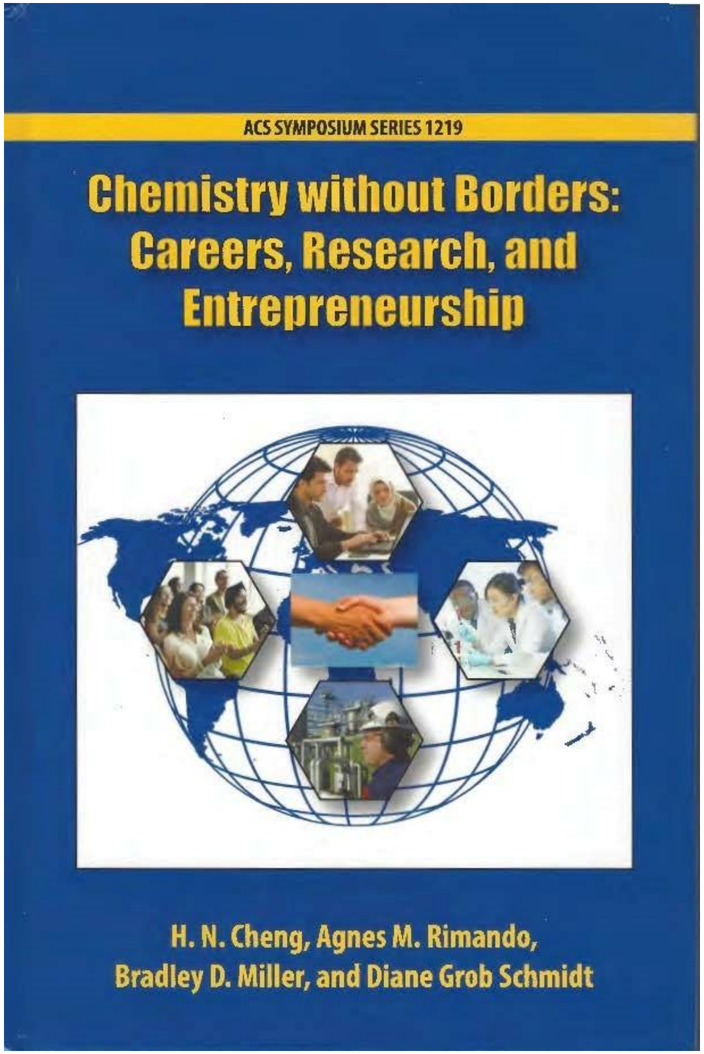
Participants of the ICSCT-AGFD symposium (Bangkok, 2014)

Receipt of the P3 Award, 2014

International Entrepreneurship: How to Start a Business and Thrive in the Global Marketplace, 2015

- Presidential symposium, held at the Fall ACS national meeting in Boston in 2015
  - Organized by Agnes Rimando and H. N. Cheng
- Initiated by 2015 ACS President Diane Grob Schmidt
  - To inform ACS members of the opportunities and the know-how relating to entrepreneurship in the international context
- 10 successful entrepreneurs spoke about their experience and provided valuable advice
  - Included George Whitesides (Harvard), Joe DeSimone (UNC), Javier Garcia Martinez (Spain), Frank Jaksch (U.S.), Thais Guarantini (Brazil), and Sharon Vercellotti (U.S.)
- 2 speakers provided valuable information
  - Factors contributing to venture success (Judy Giordan)
  - Alabama entrepreneurship program (Dan Daly)

Symposium book



- Following the successful symposium, an ACS book was edited
- Agnes was very diligent in getting the speakers to submit their chapters
- The book consisted of 19 chapters
  - 8 chapters were on international education and research
  - 10 chapters were on international entrepreneurship
  - One chapter was the overview

Building Opportunity Out of Science and Technology (BOOST), Thailand, 2015

- The first BOOST workshops (with US State Department funding) were held in 2013 for young scientists, engineers, and technologists in Indonesia and Malaysia
  - Topics covered soft skills training. Two rounds of training included 700 participants (1st round) and 32 trainers (2nd round)
- In 2015 a second round of funding was approved by US State Department for BOOST workshops in 6 cities in Thailand
  - This program also consisted of two rounds of training: 1st round in June and 2nd round in September
- Several people from IAC and from ACS International Chapters served as facilitators
  - Agnes was part of the team going to Thailand in both rounds
  - She did a great job. She facilitated the workshop on “Publishing your Research”

BOOST, Thailand, 2015

AGFD Symposium on "Chemistry of Korean Foods and Beverages", 2017

- This was the first AGFD symposium on regional foods
- It was held at the Spring 2017 ACS National Meeting in San Francisco
- Organized by Agnes Rimando (IAC) and Choon H. Do (South Korea International Chapter)
- Topics included
  - Identification and quantitative analysis
  - Elucidation of mechanism of action
  - Clinical studies involving Korean food constituents
  - Chemical aspects of nutrients & bioactive components
  - Food processing
  - Biochemistry, physiology, and microbiology of food
  - Food additives, flavors, quality and safety

AGFD Symposium On "Chemistry of Korean Foods and Beverages", 2017

Asia Pacific International Chapters Conference, 2017

- The first ever AP International Chapters Conference was held at Jeju, South Korea on Nov. 5-8, 2017
- It was organized by IAC and 10 ACS International Chapters in the AP region
  - IC's included Australia, Beijing, Hong Kong, India, Malaysia, Shanghai, South Korea, SW China, Taiwan, and Thailand
  - Ellene Tratras Contis (IAC Chair) served on the Scientific Advisory Committee, and Agnes Rimando was Chair of the Program Committee
- The program covered 9 key areas of chemistry
  - Two plenary talks by Sir Fraser Stoddart (Nobel Laureate) and Dr. Allison Campbell (2017 ACS President)
  - Also, 127 talks, 72 posters, and 10 student competition talks
- The goal of the conference was to accelerate innovation-based knowledge via ACS regional partnerships
  - Provided opportunities for AP members to showcase their research, network with one another, and provide collaborations
  - Facilitated interactions between AP chapters and between chapters and their members

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Asia-Pacific

International Chapters Conference

NOVEMBER 5-8, 2017

International Convention Center JEJU, Jeju, Korea

Plenary Speakers

Read more >

SIR J. FRASER STODDART (2016 Nobel Laureate)

DR. ALLISON CAMPBELL

2017 ACS President, Dr. Allison Campbell joins our conference!

Apply for student travel support

Cash award for student poster and oral presentation winners

Conclusions

- Agnes had the wonderful combination of creativity, enthusiasm, organizational skills, and leadership that is valued by any organization
- She had contributed much to the global chemistry enterprise:
  - Her scientific contributions were impeccable
  - Her ACS involvements were impactful
  - Her international contributions were important and consequential
- She will be solely missed!

Acknowledgments

- Lucy Yu
- Mike Appell
- Ellene Tratras Contis

Inactivation of pathogenic bacteria, fungi, and protozoa by phenolic and other natural compounds

Christina Tam

USDA-ARS-WRRC

Agnes Rimando Memorial Symposium, ACS San Diego

08-27-19

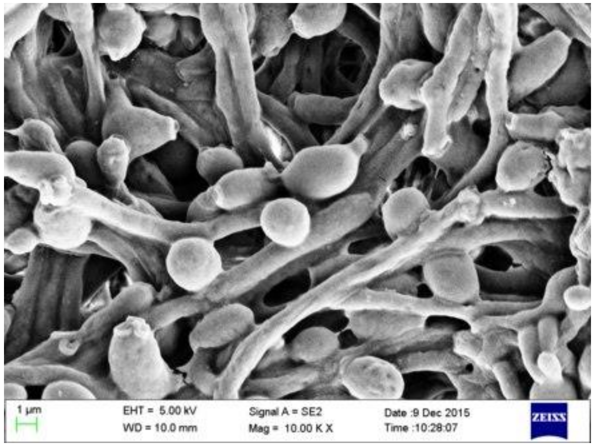
Pathogenic trichomonads

- Anaerobic, flagellated protozoan parasites
- *Trichomonas vaginalis* is the causative agent of trichomoniasis (human disease)
- *Tritrichmonas foetus* causes disease in cows (bovine) as well as cats (feline)
- WHO estimates ≅ 160 million people are infected by *T. vaginalis* annually
- Treatment with metronidazole or tinidazole
- Drug resistance is of grave concern

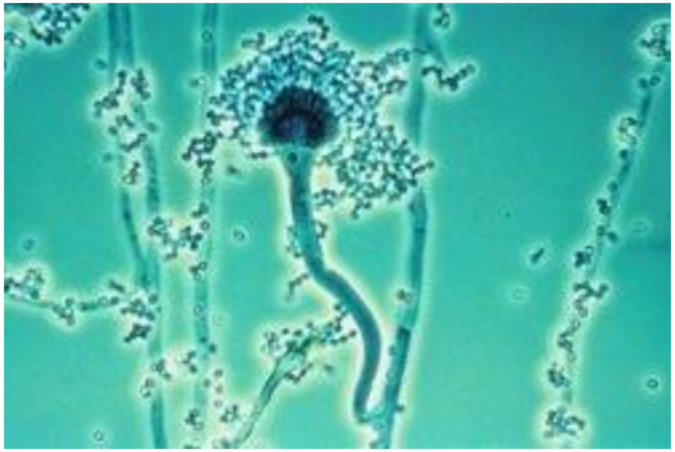
T. vaginalis

Fungal pathogens

Candida albicans

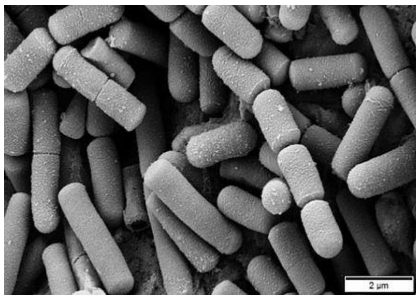


Aspergillus fumigatus

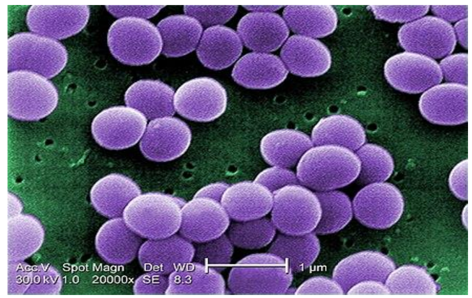


Pathogenic and non-pathogenic bacteria

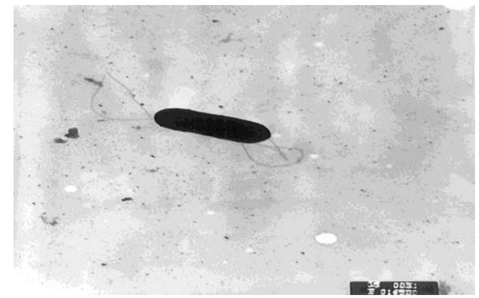
Bacillus cereus



Staphylococus aureus

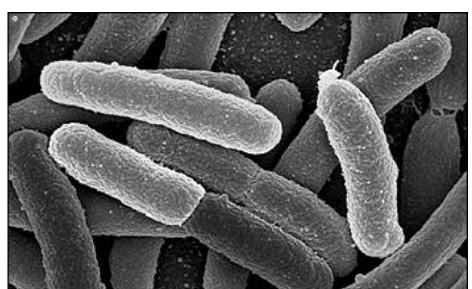


Listeria monocytogenes

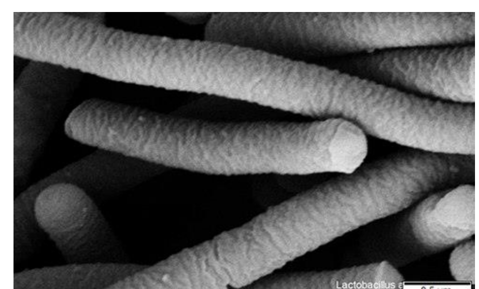


Salmonella enterica

Escherichia coli K-12



Lactobacillus acidophilus



The effect of phytochemicals (theaflavins) on the growth of pathogenic trichomonads

Theaflavin inhibits growth of human (G3) and bovine (D1) parasites

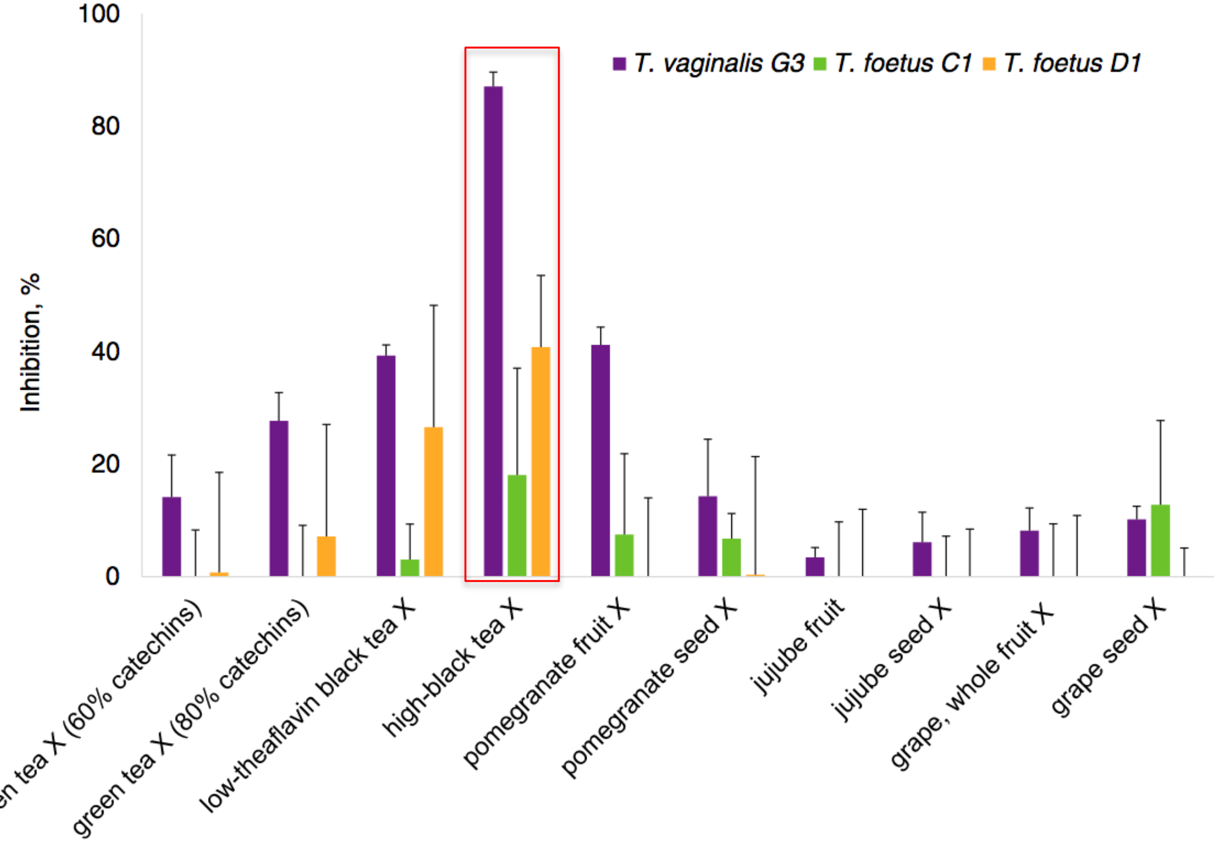


Fig. 1 Inhibitory activity of ten plant preparations with the standard error (n = 3 or higher) on three different pathogenic trichomonads (*T. vaginalis* G3, *T. foetus* C1, and *T. foetus* D1). See Table 1 for sample sources. X denotes extract

Theaflavin content in extracts

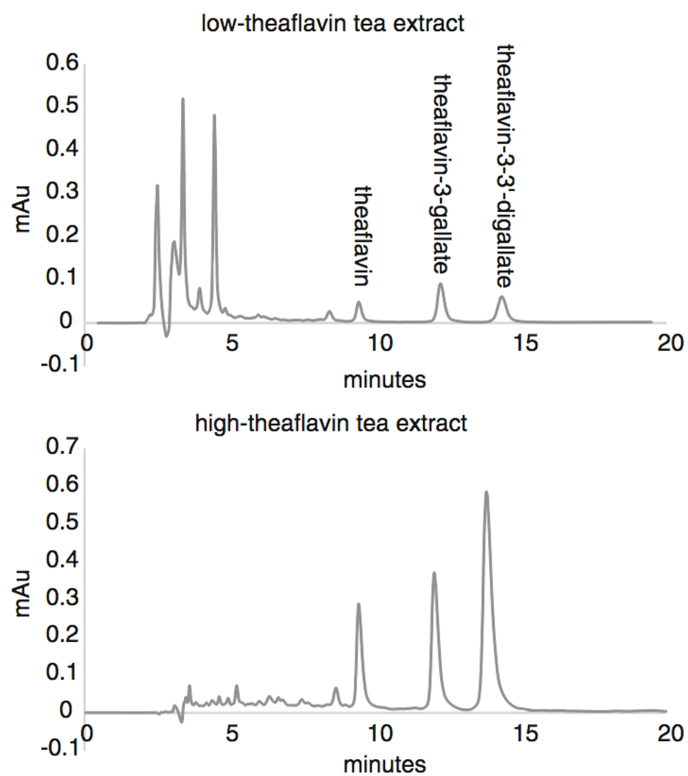


Fig. 2 HPLC of theaflavin-containing black tea extracts. The equivalent of 20 μg of powder extract was injected onto the HPLC column for each chromatogram

Table 3 Theaflavin content of the two black tea extracts evaluated in the present study, determined by HPLC analysis

	Low-theaflavin black tea extract	High-theaflavin black tea extract
Theaflavin (TF)	2.30 ± 0.13	15.3 ± 1.0
Theaflavin-3-gallate (TF3G)	6.39 ± 0.18	25.2 ± 1.2
Theaflavin-3,3-digallate (TF33G)	5.35 ± 0.21	51.7 ± 2.5
Total theaflavins	14.04 ± 0.50	92.2 ± 4.7

n = 3 for low theaflavin black tea extract, *n* = 2 for high-theaflavin black tea extract. Listed values are in % (w/w)

Antibiotic-resistant clinical parasitic strains are also sensitive to theaflavins

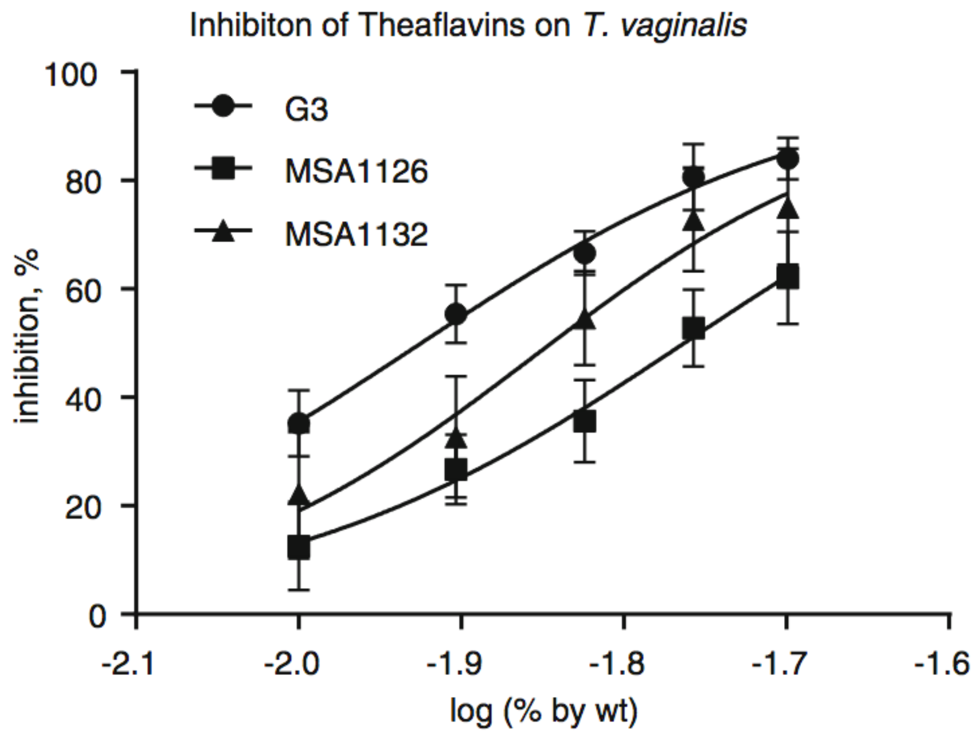
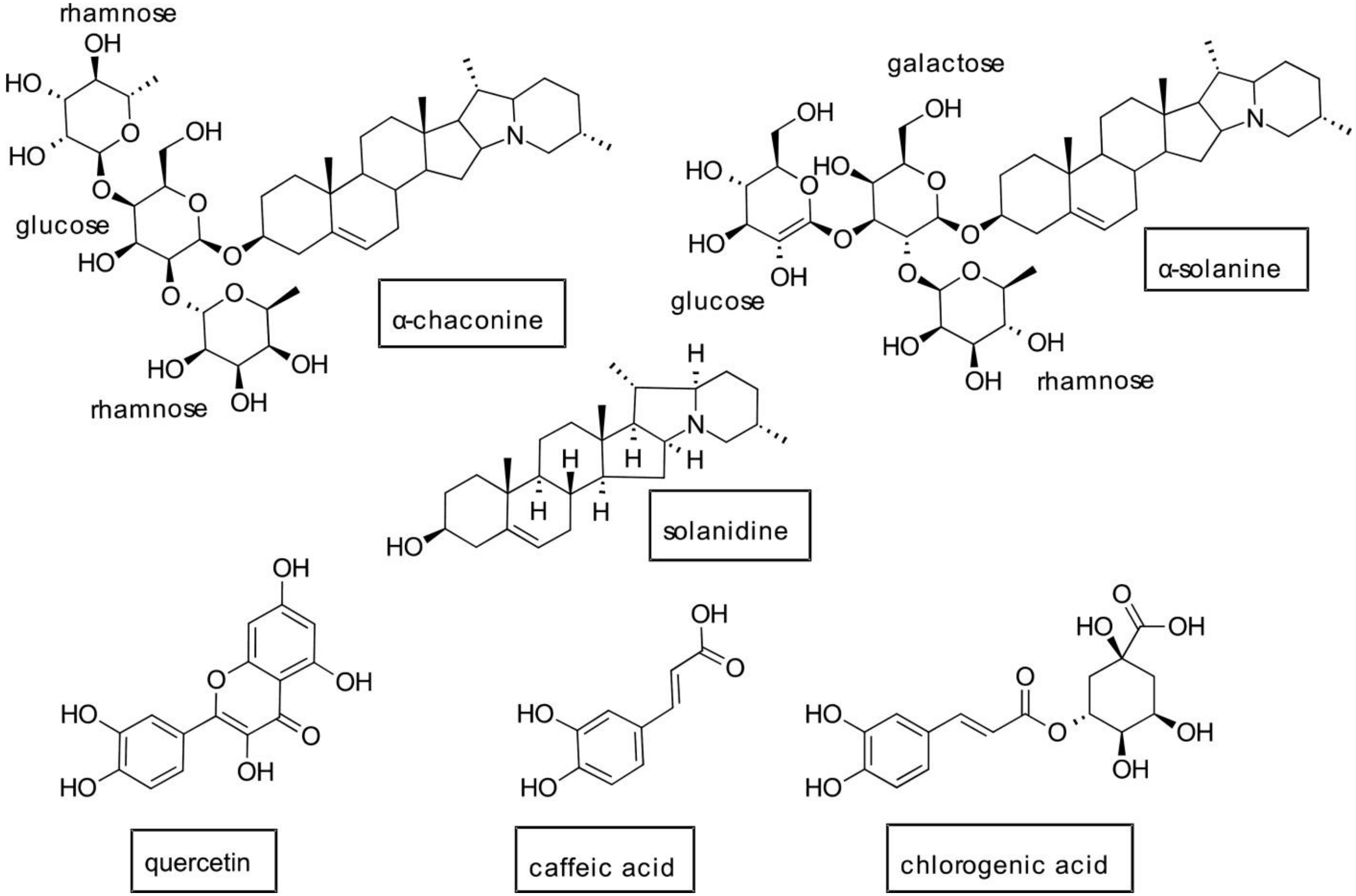


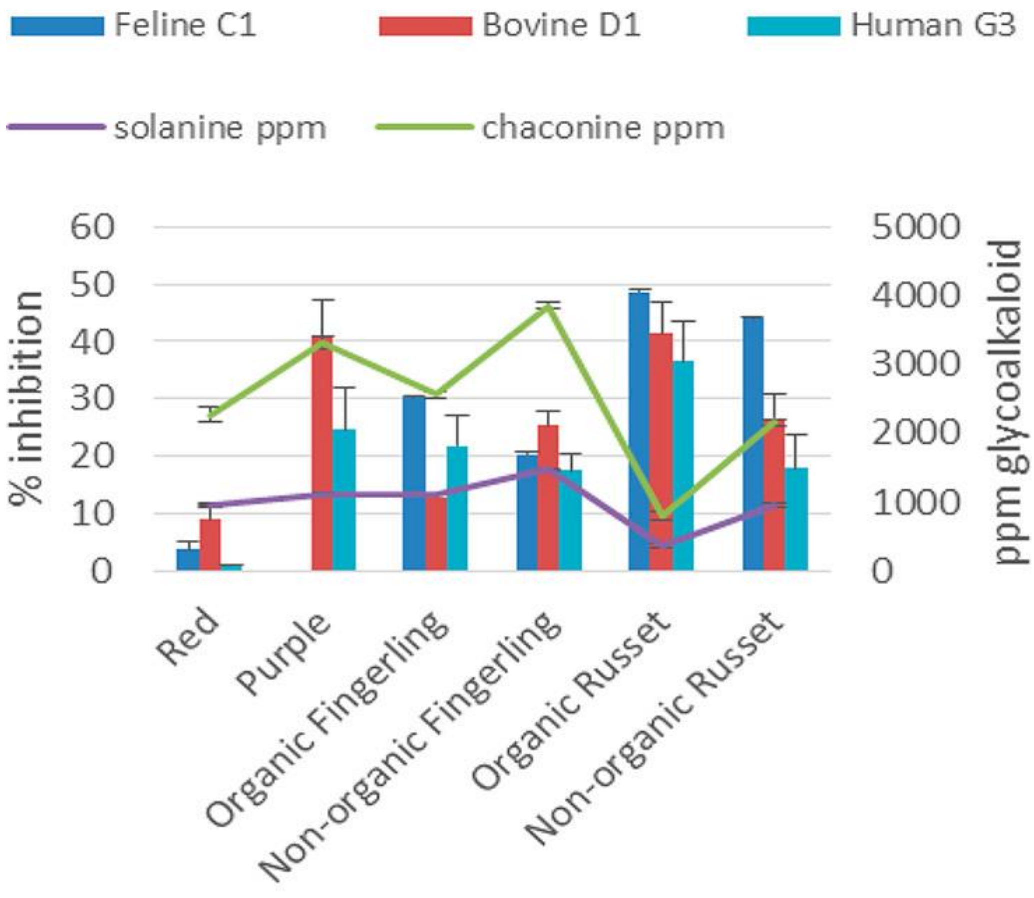
Fig. 4 Dose-dependent response of theaflavin-rich black tea extract on three different *Trichomonas vaginalis* isolates; genome strain G3, metronidazole-resistant strain MSA1126, and cytoadherent clinical strain MSA1132

Phenolic and glycoalkaloids in potato peels are anti-parasitic

Structures of the potato trisaccharide glycoalkaloids α-chaconine and α-solanine, their common aglycone alkaloid solanidine lacking the carbohydrate side chain, and the phenolic compounds caffeic and chlorogenic acids and the flavonoid quercetin



Trichomonad-inhibitory trends induced by the potato glycoalkaloids α-chaconine and α-solanine



Potato Peel Activity against Trichomonads

Parasitic growth inhibition by phenolic and glycoalkaloid compounds

Table 1. General Screening of Pure Compounds (100 μM) Reported as % Inhibition and Calculated IC_{50} Values for the Inhibition of Three Protozoan Parasites by Potato Phenolic Compounds and Potato Alkaloids

	T. fetus feline C1		*T. fetus* bovine D1		*T. vaginalis* human G3	
compound	% inhibition	IC_{50}	% inhibition	IC_{50}	% inhibition	IC_{50}
caffeic acid	21.1 ± 5.1		43.7 ± 9.0		42.8 ± 3.5	
chlorogenic acid	21.9 ± 5.9		12.1 ± 6.2		11.4 ± 6.8	
quercetin	8.5 ± 2.2		18.9 ± 1.9		45.6 ± 1.6	
solanidine	22.6 ± 5.0		22.96 ± 6.1		48.4 ± 2.2	
α-solanine	100	12.55 μM	100	10.86 μM	100	15.81 μM
α-chaconine	100	51.46 μM	100	35−60 μM	100	3560 μM

Tomato Glycoalkaloids and their anti-parasitic, anti-microbial, and anti-fungal effects

Glycoalkaloids

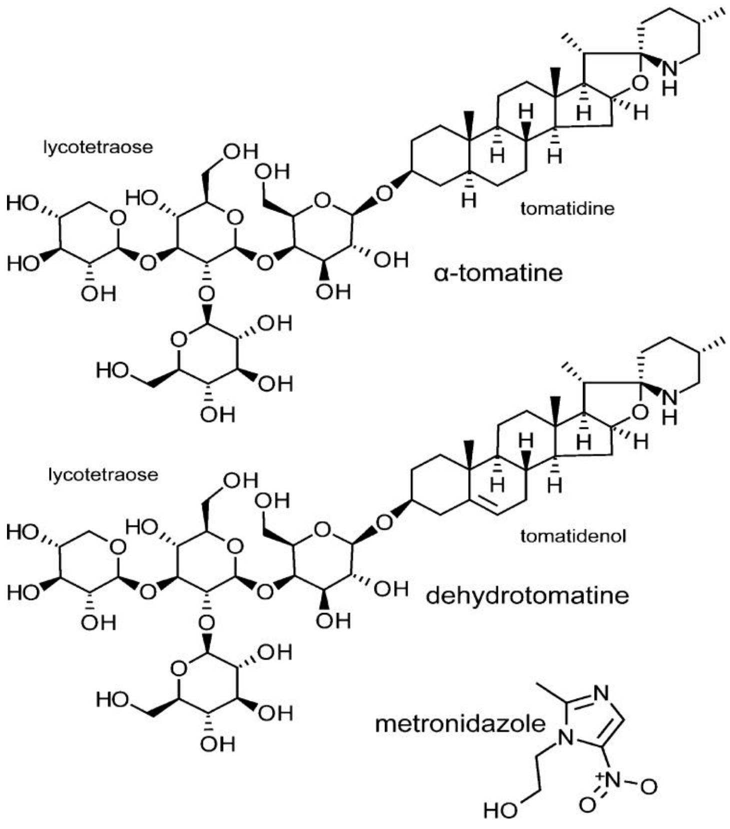


Table 1. General Screening Data for Tomatine and Tomatidine HCl on *T. vaginalis* Strain G3 and *T. foetus* Strains D1 and C1

	inhibition (%)	
	tomatine	tomatidine HCl
T. vaginalis G3	100	3.2
T. foetus D1	100	22.86
T. foetus C1	100	10.21

Inhibition of Trichomonads

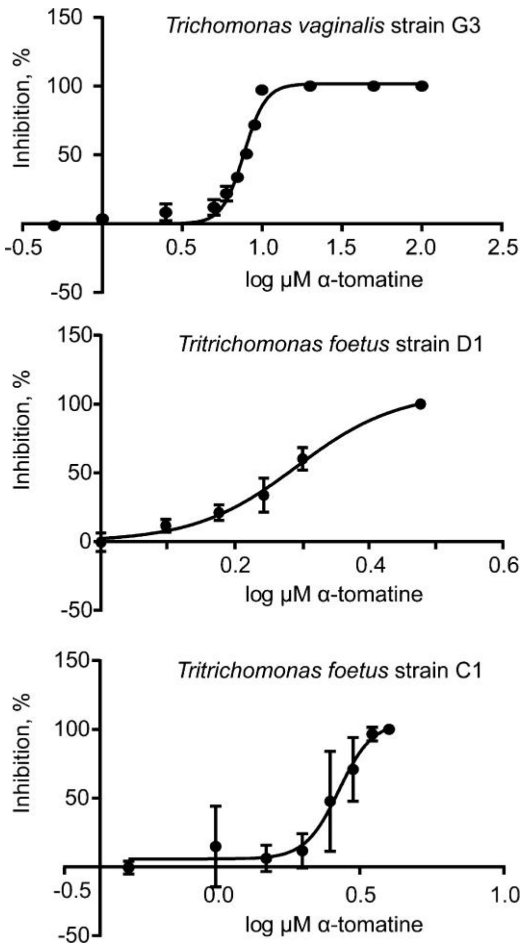


Table 2. Calculated IC_{50} Values for the Inactivation of Three Protozoan Parasites by Tomatine Compared to the Medicinal Drug Metronidazole

	IC_{50} (μM)	
	tomatine	metronidazole
T. vaginalis G3	7.9	0.72
T. foetus D1	2.7	0.49
T. foetus C1	2.0	0.55

Conclusions

- High concentration of theaflavin containing black tea exhibits anti-parasitic activity
- Potato glycoalkaloids are effective in inhbiting parasite growth
- Tomato glycoalkaloids are inhibitors of parasitic growth

Acknowledgements

- Dr. Mendel Friedman
- Dr. Luisa W. Cheng
- Dr. Jong Heon Kim
- Carol E. Levin

USDA Agricultural Research Service

www.ars.usda.gov

UNIVERSITY OF THE PACIFIC

- Dr. Kirkwood M. Land

Agnes Rimando

Memorial Symposium in honor of the Scientist & International Ambasdsador of Agricultural & Food Chemistry

By Kanjana Mahattanatawee
ACS Fall Meeting, San Diego, CA
August 27, 2019

March 4-5, 2014

1st Joint ACS AGFD-ACS ICSCT Symposium on Agricultural and Food Chemistry, Bangkok, Thailand

November 5-8, 2019

APICC 2017 : Asia-Pacific International Chapter Conference, Jeju, Korea

2014

2015

2017

June 22 – July 2, 2015

BOOST Workshop (Building Opportunity Out of Science and Technology) Thailand

October 11-16, 2015

BOOST Trainer Leadership Institute, Chiang Mai, Thailand

2014

http://www.acsthailand2014.siam.edu/

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1st Joint ACS AGFD – ACS ICSCT Symposium on Agricultural and Food Chemistry

March 4-5, 2014, Bangkok, Thailand

Organized by
The American Chemical Society International Chemical Sciences Chapter in Thailand (ACS-ICSCT) and ACS Agricultural and Food Chemistry Division (ACS-AGFD)

Proceedings of the 1st Joint ACS AGFD- ACS ICSCT Symposium Thailand, March 4-5, 2014

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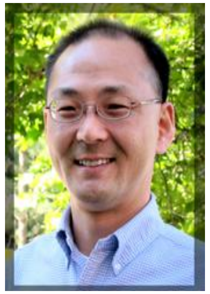




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Partners for Progress & Prosperity Award

from ACS President, Marinda Wu

at the ACS National meeting in San Francisco, August 10, 2014


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Presented to

International Chemical Sciences Chapter in Thailand

in recognition of

the successful first joint AGFD – ICSCT Symposium on Agricultural and Food Chemistry in Bangkok, Thailand

Awarded August 10, 2014
248th National ACS Meeting
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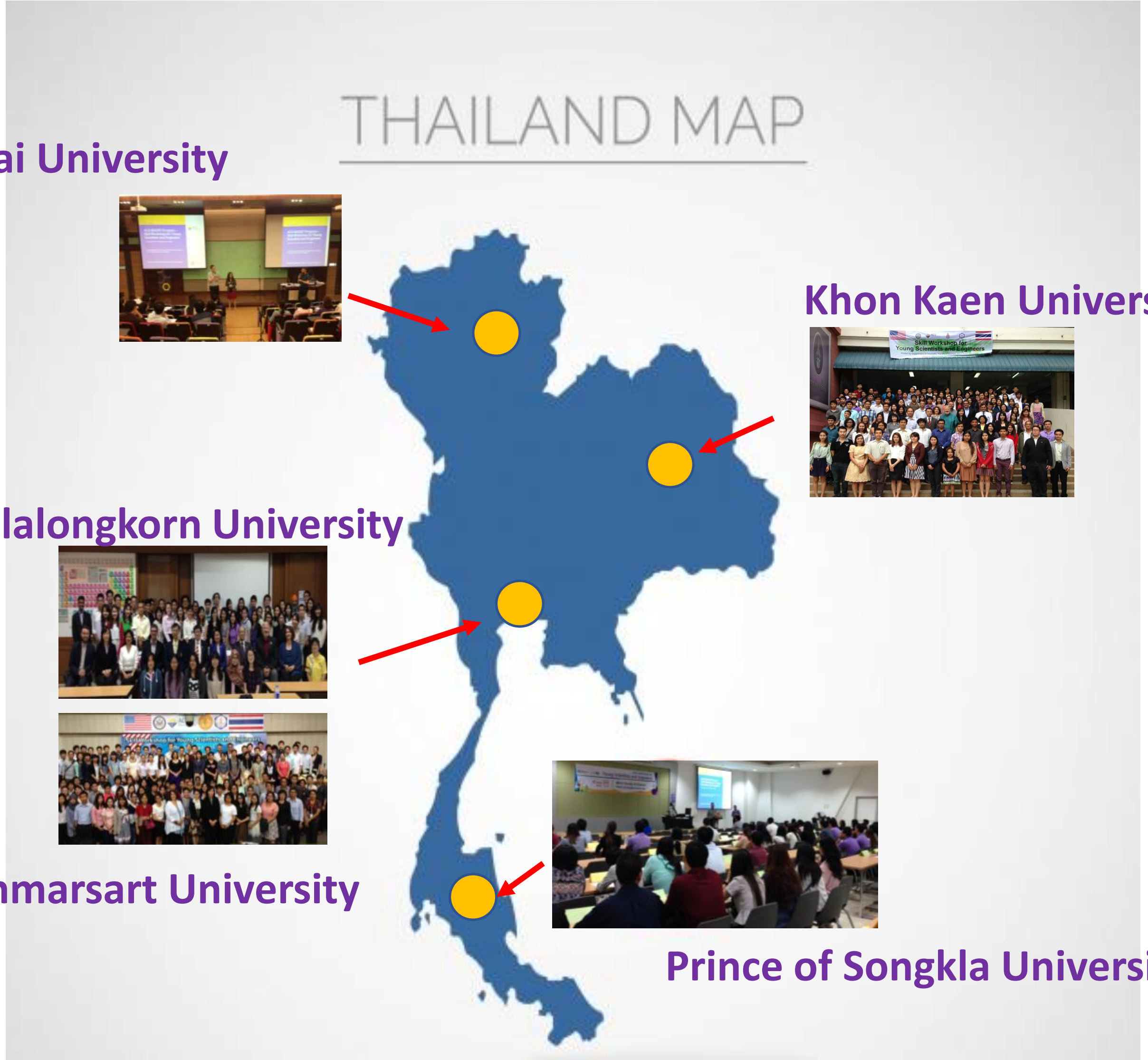
2015

BOOST Workshop
(Building Opportunity Out of Science and Technology)



2015

BOOST Workshop, June 22 – July 2, 2015, Thailand

1. Chulalongkorn University
2. Khon Kaen University
3. Chiang Mai University
4. Prince of Songkla University
5. Thammarsart University

2015

BOOST Workshop
(Building Opportunity Out of Science and Technology)

2015

BOOST Trainer Leadership Institute

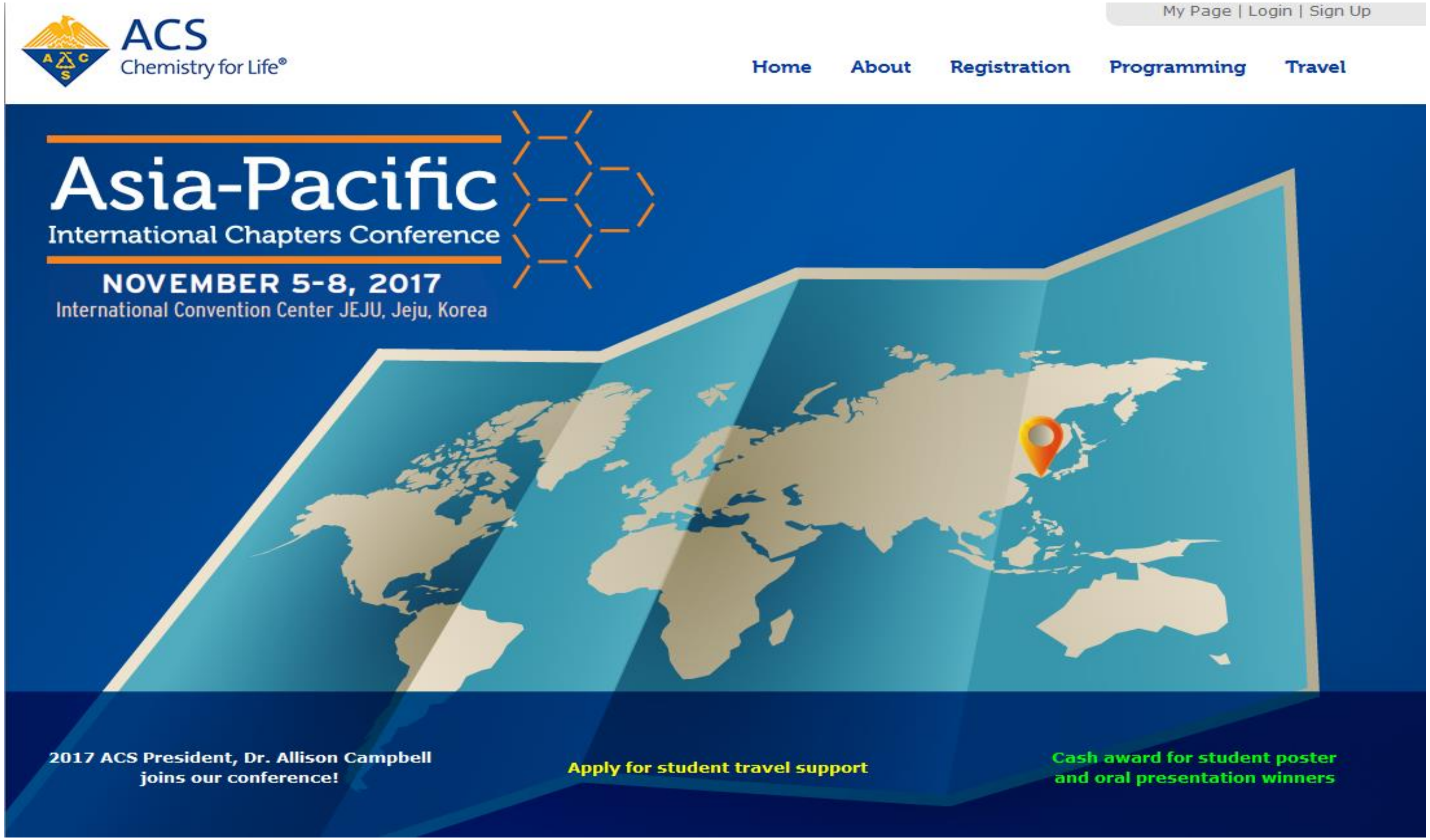
11-16 October, 2015

Le Meridien Hotel , Chiang Mai, Thailand

2017

November 5-8, 2019

APICC 2017 : Asia-Pacific International Chapter Conference, Jeju, Korea



2017

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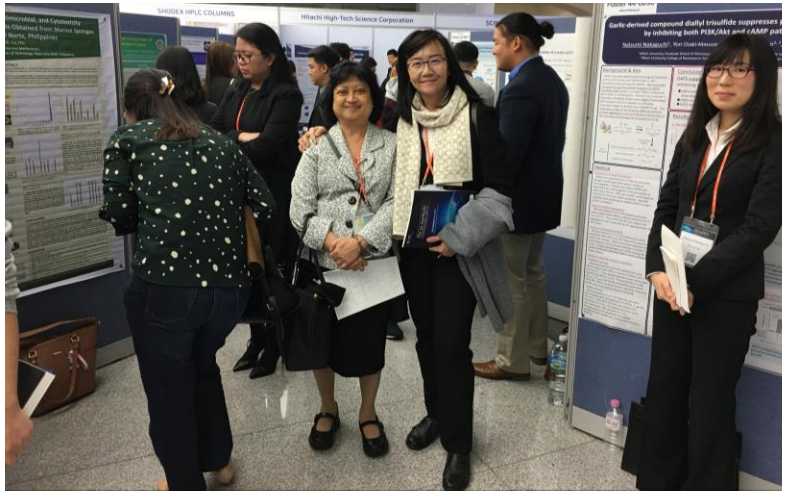
APICC 2017 : Asia-Pacific International Chapter Conference, Jeju, Korea



Friendship : Agnes with her family in Thailand

Friendship

My last picture with Agnes
in Jeju, Korea, 2017.

She is my dear friend and always in my memory.

I miss you Agnes!

Methods for identifying and characterizing health-promoting compounds in fruit and other agricultural products:

A tribute to the work of Dr. Agnes Rimando

Lauren S. Jackson, Ph.D.
U.S. Food and Drug Administration
Division of Processing Science & Technology
Institute for Food Safety & Health
6502 S. Archer Rd.
Bedford Park, IL 60501

ACS Fall Meeting, San Diego, CA

Tuesday, August 27, 2019

FDA CFSAN

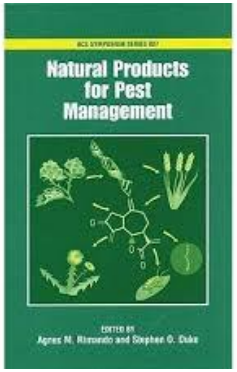
ILLINOIS INSTITUTE OF TECHNOLOGY

IFSH INSTITUTE FOR FOOD SAFETY AND HEALTH

Career of Dr. Agnes Rimando

- B.S. and M.S. - University of Philippines- Pharmacy
- Ph.D. - University of Illinois at Chicago- Pharmacognosy
- Post Doctoral Fellow- University of Illinois at Chicago (1994-96)
- Post Doctoral Fellow- USDA/ARS- Toxicology and Mycotoxin Research Center, Athens, GA (1996)
- Research Chemist- USDA/ARS-National Products Utilization Research Center, Oxford MS (1996-2018)

- Published >150 research papers, abstracts and presentations



- Membership in many scientific societies such as ACS, American Council for Medicinally Active Plants, American Society for Pharmacognosy, International Alleopathy Society and others

- Service and Leadership in ACS (Chair of AGFD; Chair of ACS-Ole Miss Local Section; ACS AGFD Councilor; ACS National Awards Committee)

- Award Recipient: ACS Fellow; ACS/AGFD Fellow; ACS/AGFD Distinguished Service Award; USDA ARS Mid South Area Senior Scientist of the Year; ACS Ole Miss Section Researcher of the Year; FAS and U.S. Embassy Rwanda Science Fellow

Research Focus at Natural Products Utilization Research Center

Natural products for weed management

Strategies to prevent off-flavors and diseases in fish from aquaculture

Natural Products Utilization Research Center (USDA/ARS)

Eliminate arthropod vectors and the diseases that they transmit

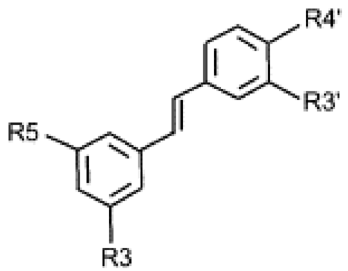
Product quality and new uses

Dr. Agnes Rimando's Research on Health Promoting Compounds in Plant Products

Stilbenes

- Naturally occurring polyphenolic compounds found in fruits and other plants
- Secondary metabolites involved in plant responses to various biotic and abiotic stresses
- Have been shown to exhibit diverse biological effects

stilbene	occurence	R3	R5	R3'	R4'
trans-resveratrol	*Vitis, Arachis, Fallopia*	OH	OH	H	OH
trans-piceid	*Vitis*	OGlu	OH	H	OH
pinosylvin	*Pinus,*	OH	OH	H	
piceatannol	*Picea*	OH	OH	OH	OH
pinosylvin monomethylether	*Pinus, Alnus*	OCH_3	OH	H	OH
trans-pterostilbene	*Vitis, Vaccinium*	OCH_3	OCH_3	H	OH
astringin	*Picea*	OGlu	OH	OH	OH
rhapontin	*Rheum*	OGlu	OH	OH	OCH_3



Identification, Isolation and Characterization of Stilbenes in Vaccinium Berries

- Identification and quantitation of stilbenes in vaccinium berries (blueberries, cranberry, deer berry, lingonberries)
- Determined HPE of stilbenes
  - Pterostilbene reduces plasma lipoproteins and cholesterol
  - PterostilbeneiInhibits colon cancer progression and inhibits other types of cancers
  - Evaluated behavioral effects of resveratrol analogs-implications for aging
  - Molecular pathways affected by pterostilbene
- Developed ways to improve production of resveratrol and other stilbenes (production and secretion of resveratrol in hairy root cultures of peanut)

Identification, Quantitation and Characterization of Bioactives from Plants

American Skullcap (*Scutellaria lateriflora*)

- Native to North America, but it is now widely cultivated elsewhere
- Used as a medicinal plant for >200 years as a relaxant
- Has antioxidant properties
- Major flavonoids include scutellarein, baicalin, baicalein, and chrysin
- Research by Rimando and colleagues determined the effect of timing and frequency of harvest and fertilizers on shoot yield and flavonoid content of American skullcap
  - There was no difference in yield or flavonoid content between early or late harvest
  - Greenhouse experiments were conducted to determine the effects of nitrogen (N), phosphorus (P), and potassium (K) fertilizer on biomass yield and flavonoid content of American skullcap (*Scutellaria lateriflora*).

Identification, Quantitation and Characterization of Bioactives from Plants

Serviceberry or Saskatoon Berry

- Native to the North Glacier forests of the Rocky Mountains in Montana
- Tea brewed from serviceberry twigs and leaves used by Blackfeet Indian tribe to treat diabetes and certain cancers
- Cyanidin-based anthocyanins (cyanidin-3-O-galactoside, cyanidin-3-O-glucoside, cyanidin-3-O-arabinoside, and cyanidin-3-O-xyloside) make up the major phenolic constituents in serviceberries;
- Prunasin, quercetin- and kaempferol-derived glycosides, hydroxycinnamic acids, catechins, and some neolignans are founds in serviceberry leaves.

Identification, Quantitation and Characterization of Bioactives from Plants

Serviceberry or Saskatoon Berry

- Research by Rimando and colleagues from Auburn University identified potential antidiabetic mechanisms of serviceberry
  - Serviceberry leaf extracts and subfractions demonstrated potent inhibitory activity against mammalian intestinal alpha-glucosidase activity
  - in an animal model, serviceberry leaf subfraction demonstrated significant inhibition of intestinal α-glucosidase activity, and delayed the absorption of carbohydrates, resulting in significant lowering of post-prandial blood glucose concentrations, similar to the antidiabetic drug Acarbose™

Publications on Bioactives in Plants

Poulose, S.M.; Fisher, D.R.; Bielinski, D.F.; Gomes, S.M.; **Rimando, A.M**.; Schauss, A.G.; Shukitt-Hale, B. Restoration of stressor-induced calcium dysregulation and autophagy inhibition by polyphenol-rich acai (Euterpe spp.) fruit pulp extracts in rodent brain cells *in vitro*. *Nutrition* 30(7-8), 853-862, 2014.

Shiwakota, S.; Shannon, D.A.; Wood, C.W.; Lawrence, K.S.; Kemppainen, B.; Joshee, N.; **Rimando, A.** Nitrogen, phosphorus and potassium effects on biomass yield and flavonoid content of American skullcap (*Scutellaria lateriflora*). Journal of Plant Nutrition.
Mizuno, C.; Schrader, K.; **Rimando, A.M.** Algicidal activity of stilbene analogs. *J. Agric. Food Chem*. 56, 9140-9145, 2008.

Shiwakoti, s.; Shannon, D.A.; Wood, C.W.; Lawrence, K.S.; Kemppainen, B.; Joshee, N.; **Rimando, A.M.** Harvestig number and timing effects on shoot yield and flavoinoid content in American skullcap (*Scutellaria lateriflora*). *Journal of Herbs, Spices and Medicinal Plants*. 19(3), 248-261, 2013

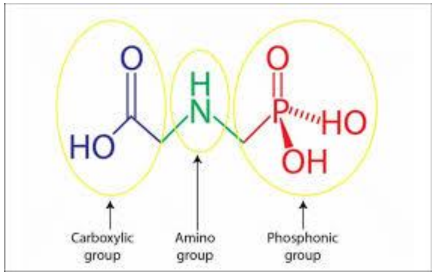
Zhang, A.J.; **Rimando, A.M**.; Dhar, S.; Mizuno, C.S.; Penman, A.D.; Evenson, A.S. Serviceberry [*Amelanchier alnifolia* (Nutt.) Nutt.ex.M.Roem (Roseae)] leaf extract inhibits mammalian alpha-glucosidase activity and suppresses postprandial glycemic response in a mouse model of diet-induced obesity and hyperglycemia. *Journal of Ethnopharmacology*. 143(2), 481-487, 2012.

Need for Weed Management in Agriculture

- About 13% of the world's crops are lost due to damage caused by weeds each year
- Crop yields have increased due to development of weed control technologies such as transgenic crops and synthetic herbicides.
- Herbicide resistance and the sensitivity of the public to the use of synthetic herbicides have resulted in the demand for safer and more efficacious herbicides.
- Glyphosate is one of the most widely used herbicides
  - Acts by inhibiting aromatic amino acid synthesis
  - Transgenic crops have been developed with glyphosate resistance (GR)
  - Some GR crops exhibit injury when treated with glyphosate
  - Research is needed to determine cause of injury in GR crops and differences in GR in crop species

Weed Management Research- A. Rimando

- Effects of glyphosate on GR crops
  - Determined the cause of injury to GR soy is due to a metabolite of glyphosate (aminomethylphosphonic acid)
  - Identified mechanisms by which crop species have differing resistance to glyphosate
  - Found that glyphosate treatments did not affect production of isoflavones in GR soy
  - Neither glyphosate nor the GR transgene affected the content of the minerals measured in leaves and seed, harvested seed amino acid composition, or yield of GR soybean



Glyphosate

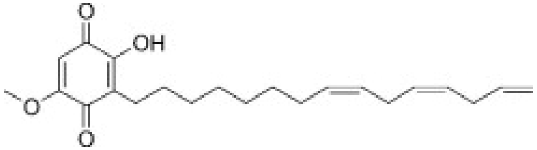
Need for Weed Management in Agriculture

Allelopathy- inhibition of growth of a plant through the production of phytotoxins released by another plant.

- Crop plants exhibiting allelopathic effects
  - Rice, wheat, oats, sunflower, barley and sorghum
- Allelopathic compounds could be used to prevent growth of undesirable plant species (i.e. weeds) or crop cultivars that produce allelopathic compounds could be chosen
- Research is needed on identifying the compounds, pathways and genes involved in biosynthesis of allelopathic compounds.

Allelopathic Compounds: Research by A. Rimando

- Characterized allelopathic compounds derived from sorghum (sorgoleone, resorcinolic lipids, quinones) and rice.
- Evaluated the biochemical pathways and genes involved synthesis of sorgoleone
- Measured the phytotoxic effects of synthesized resorcinolic lipid derivatives and quinones with various side chain sizes against a monocot and a dicot species.
    - The quinones were phytotoxic, whereas the resorcinolic lipids were not
    - Of the quinones, 2-hydroxy-5-methoxy-3-pentylcyclohexa-2,5-diene-1,4-dione, showed phytotoxic activity similar to that of natural compound sorgoleone.



Sorgoleone

Publications on Weed Management

Allelochemicals:

Baerson, S.R.; Dayan, F.E.; **Rimando, A.M**. et al. A functional genomics investigation of allelochemical biosynthesis in *Sorghum bicolor* root hairs. *J. Biol. Chem.* 283, 3231-3247, 2008

Dayan, F.E.; Kagan, I.A.; **Rimando, A.M**. Elicidation of the biosynthetic pathway of the allelochemical sorgoleone using retrobiosynthetic NMR analysis. *J. Biol. Chem*. 278, 28607-28611, 2003

Mizuno, C.S.; **Rimando, A.M**., Duke, S.O. Phytotoxic activity of quinones and resorcinolic lipid derivatives. *J. Agric. Food Chem*. 58, 4353-4355, 2010

Rimando, A.M.; Olofsdotter, M.; Dayan, F.E.; Duke, S.O. Searching for rice allelochemicals: An example of bioassay guided isolation. *Agronomy Journal* 93, 16-20, 2001

Rimando, A.M.; Dayan, F.E.; Streibig, J.C., PS II Inhibitory activity of resorcinolic lipids from sorghum bicolor. *J. Nat. Prod*. 66, 42-45, 2003

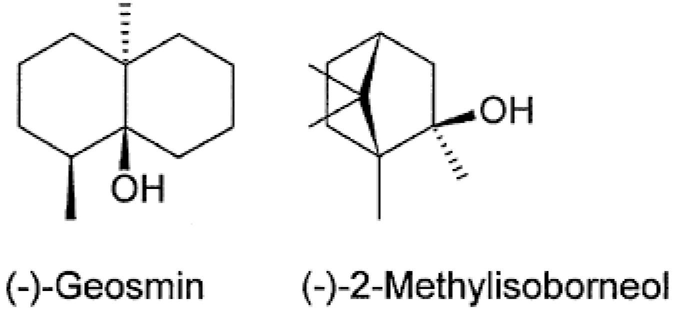
Effects of Glyphosate on GR Crops:

Nandula, V.K.; Reddy, K.N.; **Rimando, A.M.**; Duke, S.O.; Poston, D.H. Glyphosate resistant and susceptible soybean (*glycine max*) and canola (*Brassica napus*) dose response and metabolism relationships with glyphosate. *J. Agric. Food Chem*. 55, 3540-3545, 2007

Reddy, K.N..; **Rimando, A.M**.; Duke, S.O. Aminomethylphosphonic acid, a metabolite of glyphosate causes injury in glyphosate-treated, glyphosate-resistant soybean. *J. Agric. Food Chem*. 52, 5139-5143, 2004

Improvement of Aquaculture Management

- Farm-raised channel catfish is largest segment in aquaculture industry in U.S.
- Mississippi produces half of farm-raised catfish/year
- Economic losses in industry
  - Diseases such as columnaris disease
  - Musty/earthy off-flavors in fish- costs industry >$60 million/year
    - Caused by cyanobacteria- *Oscillatoria perornata*
    - Geosmin and 2-methylisoborneol (MIB)



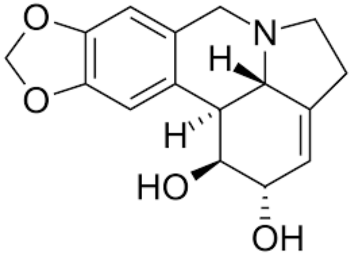
Columnaris Disease

- Caused by fish pathogen, *Flavobacterium columnare*
- Symptoms include severe gill-rotting and possible skin ulceration in catfish
- Conventional procedures to prevent columnaris
  - Medicated feeds, attenuated vaccines, nonantibiotic therapeutic agents, copper sulfate pentahydrate and potassium permanganate
  - Disadvantage of therapeutic agents- broad spectrum toxicity
- Natural compounds sought for control of columnaris

Use of Natural Compounds to Prevent Columnaris Disease

Lycorine:

- Lycorine- a pyrrolo[de]phenanthridine ring-type alkaloid extracted from various genera of plants in the *Amaryllidaceae*
- Biological properties of lycorine include inhibition of the following: (1) ascorbic acid (AA) biosynthesis; (2) growth and cell division in higher plants, algae, and yeasts; and (3) cyanide-insensitive respiration.
- 17 lycorine analogues were synthesized and evaluated for antibacterial activity against two isolates of *Flavobacterium columnare* using a rapid bioassay.
  - A carbamate analogue had the strongest antibacterial activity toward both *F. columnare* isolates.

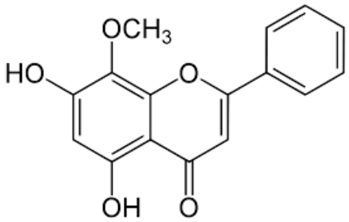


Lycorine

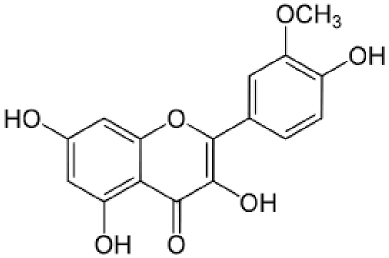
Use of Natural Compounds to Prevent Columnaris Disease

Flavones:

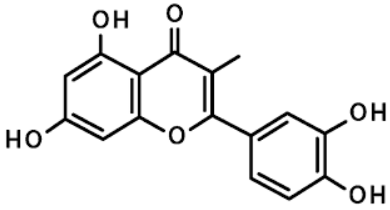
- Wogonin- flavonoid-like chemical compound which was found in *Scutellaria baicalensis*
- Tested wogonin analogs and other flavones for activity against *F. colomnare*.
- Isorhamnetin, luteolin, and biochanin A were highly toxic to F. columnare, but less so than wogonin



Wogonin



Isorhamnetin



Luteolin

Use of Natural Compounds and other Methods to Control Musty/Earthy Flavor

- Algicides are used to control cyanobacteria in fish ponds
  - Copper sulfate, chelated copper compounds, diuron (EPA approved)
  - These compounds have broad-spectrum toxicity
  - Persist in environment
- Need for natural compounds and other methods to control cyanobacteria
- Research done by Dr. Agnes Rimando and colleagues
  - Water soluble analogues of 9,10-anthraquinone reduced levels of *O. perornata* and MIB in catfish pond water
  - Stilbene derivatives- cis and trans isomers of 4-(3,5-dimethoxystyryl)aniline showed moderate and selective algicidal activity toward *O. perornata*
  - Ozonation of inlet water in recirculating aquaculture systems
  - Confirmed geosmin and MIB as the cause of earthy/musty off-flavors in cultured bass and white sturgeon

Publications on Aquaculture Management

Mizuno, C.; Schrader, K.; **Rimando, A.M.** Algicidal activity of stilbene analogs. *J. Agric. Food Chem*. 56, 9140-9145, 2008.

Schrader, K.K.; Rubio, S.A.; Piedrahita, R.H., **Rimando, A.M.** Confirmation of geosmin and 2-methylisoborneol as the cause of earthy/musty off-flavors in cultured bass (*Micropterus salmoides*) and white sturgeon (*Acipenser transmontanus*). *North Amer. J. Agriculture*. 67, 138-147, 2005.

Schrader, K.K., Tucker, C.S.; Hanson, T.R.; Gerard, P.D.; Kingsbury,S.K.; **Rimando, A.M.** Management of musty off-flavor in channel catfish from commercial ponds with weekly applications of copper sulfate. *North Amer. J. Aquaculture*. 67, 138-147, 2005.

Schrader, K.K.; Davidson, J.W.; **Rimando, A.M.;** Summerfelt, S.T. Evaluation of ozonation on levels of the off-flavor compounds geosmin and 2-methylisoborneol in water and rainbow trout *Oncorhynchus mykiss* from recirculating aquaculture systems. *Aquacultural Engineering*. 43, 46-50, 2010.

Tan, C.X.; Schrader, K.; Mizuno, C., **Rimando, A.** Activity of lycorine analogs against the fish bacterial pathogen *Flavobacterium columnare*. *J. Agric. Food Chem.* 59, 5977-5985, 2011.

Tan, C.-X.; Shrader, K.K.; Khan, I.A.; **Rimando, A.M**. Activities of wogonin analogs and other flavones against *Flavobacterium columnare. Chemistry and Biodiversity. 259-272, 2015.*


thank you
danke
gracias
merci
obrigado
bedankt
dziękuję
спасибо
謝謝
рахмат
Баярлалаа
ngiyabonga
teşekkür ederim
go raibh maith agat
mochchakkeram
sukriya
kop khun krap
terima kasih
grazie
arigatô
dakujem
takk
tapadh leat
감사합니다
ευχαριστώ
ありがとう
мерси
dank je
mauruuru
hvala
sagolun
taiku
faafetai lava
vinaka
blagodaram
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kia ora
barka
welalin
tack
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obrigada
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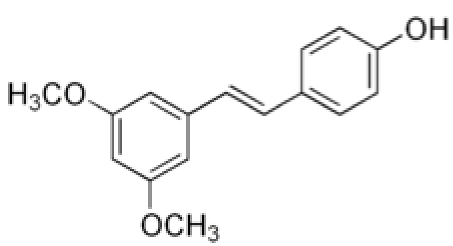
Oregon State University

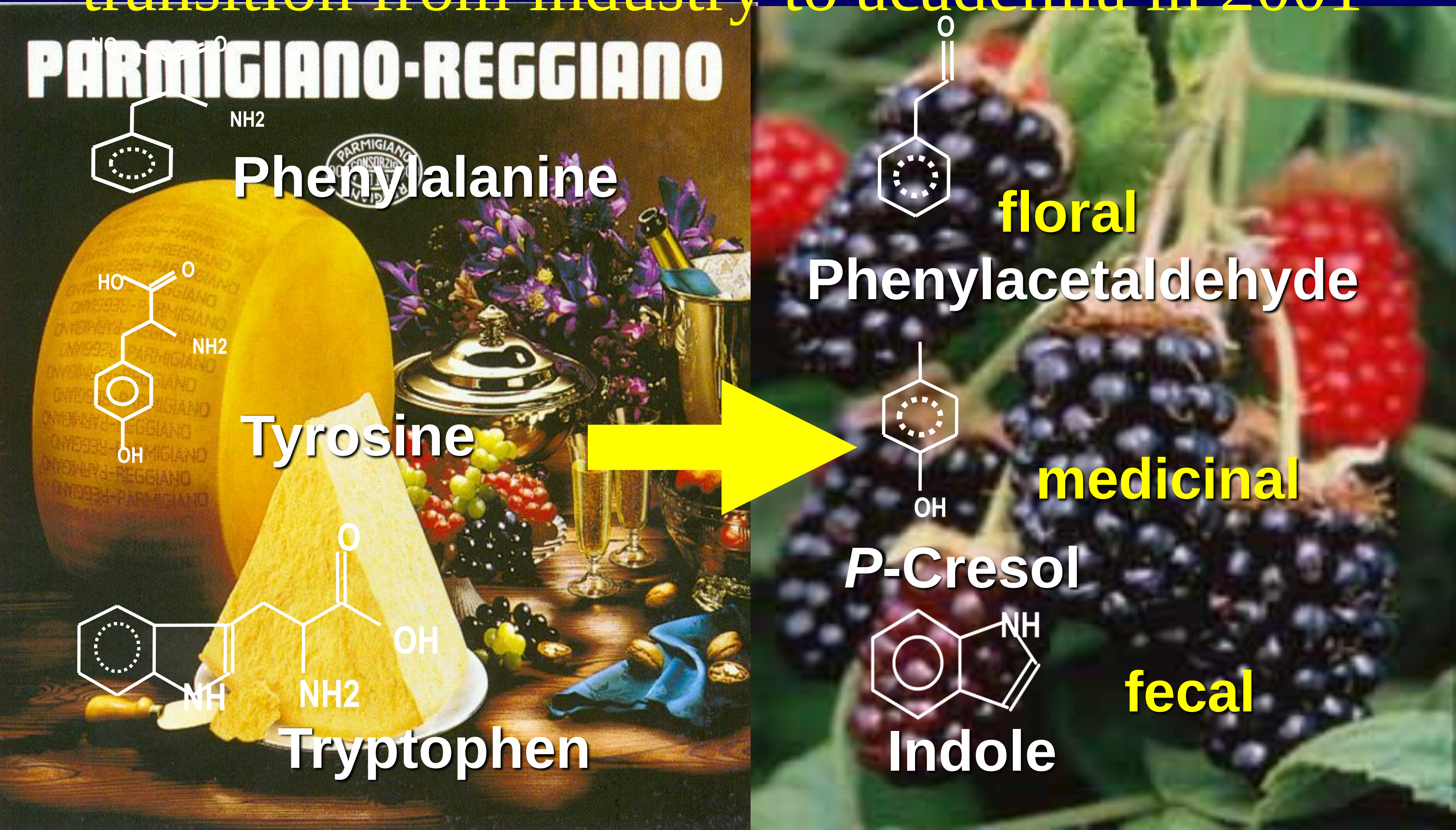
Agnes Rimando Memorial Symposium in honor of the Scientist & International Ambassador of Agricultural & Food Chemistry

Healthy and tasteful berry fruits-from pterostilbene to raspberry ketone



Michael Qian, PhD, Professor of Flavor Chemistry
Oregon State University, Corvallis, OR 97330

Interaction with Agnes at my early career transition from industry to academia in 2001



We shared research interests with Agnes in small fruits (berry fruits)

- Flavoromics-flavor chemical and biochemical formation and metabolism in food, small fruits (berries), grape and wine






Berry Fruits in Pacific Northwest

- The Pacific Northwest is the leading producer of berry fruits such as blackberry, raspberry
- Within this industry, approximately 70% of the blackberry plantings are devoted to ‘Marion’ blackberry
-

'Marion' Blackberry (*Rubus spp. hyb*)

- Gold standard for the industry
  - Productive
  - Disease resistance
  - Attractive flavor
  - Ideal fruit quality for processing
- Drawback of the plant
  - Not reliably cold hardy
  - Thorny

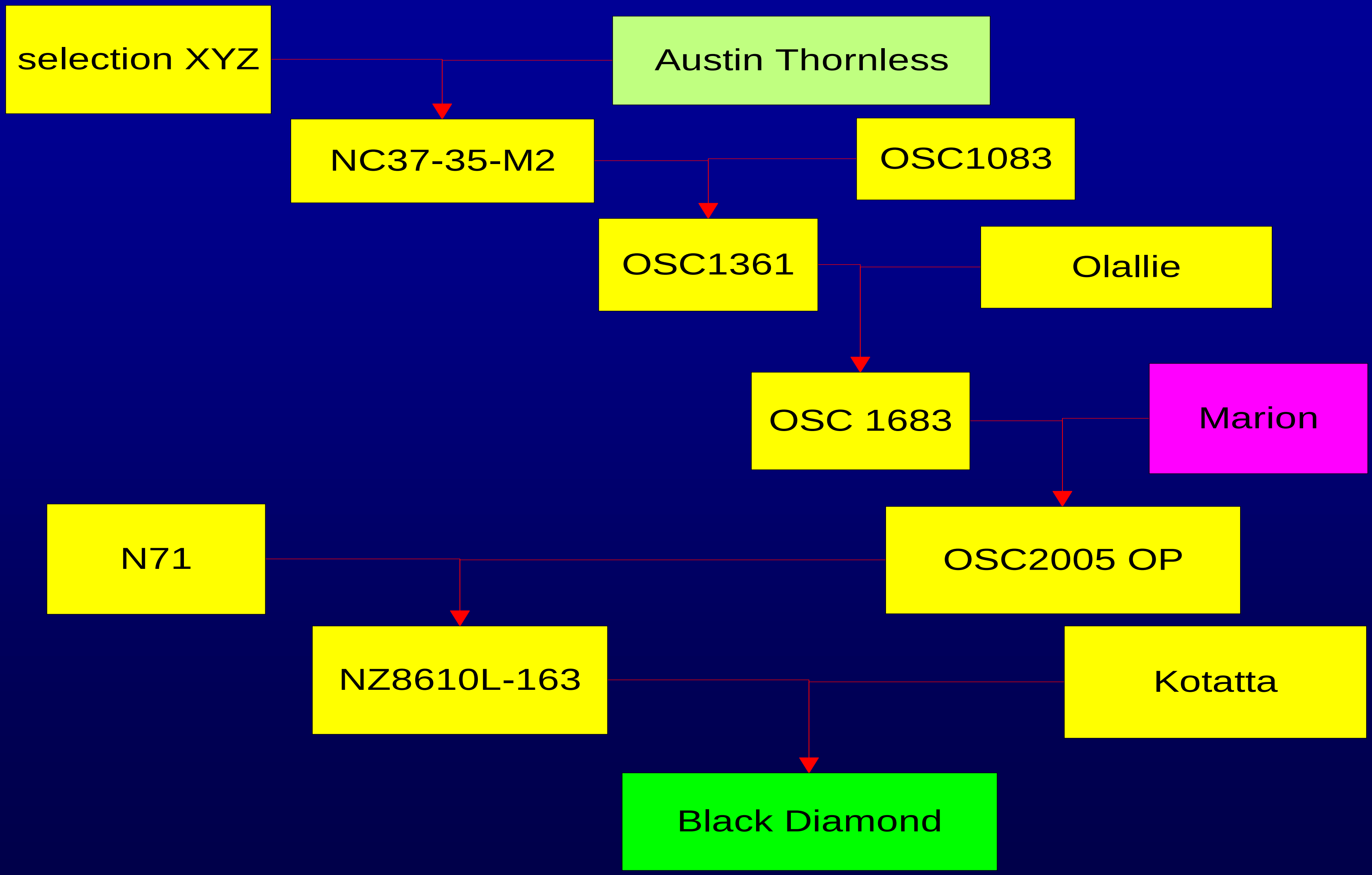
Blackberry Research Objectives in Pacific Northwest

- High yield
- Winter hardy
- Machine harvestable
- Thornless
- Superior flavor quality
  - Comparable to 'Marion' flavor

Thornless Blackberry Breeding

- Thornless blackberries were achieved through decade's breeding
- Flavor is diverse

Thornless 'Black Diamond' Pedigree



Finn *et. al.*, HortScience 40(7):2175-2178

On the Road of Developing Thornless Blackberries with 'Marion' Flavor

- Understand the flavor of the target
- Provide objective flavor evaluation during breeding process
- Guide "Flavor-directed plant breeding"

GC-Olfactometry Analysis of 'Marionberry'

Furaneol
β-Ionone
Linalool
Linalool oxide

Aldehydes
C6-alcohols
Esters

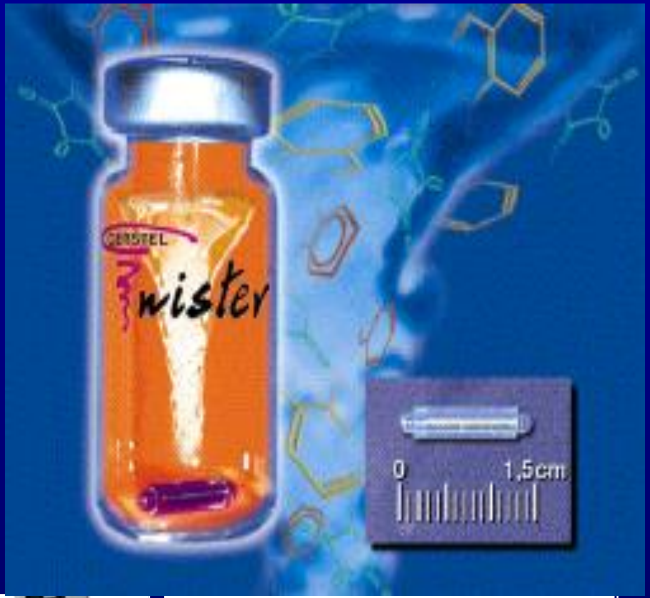
Lack of woody, spicy, herbaceous compounds

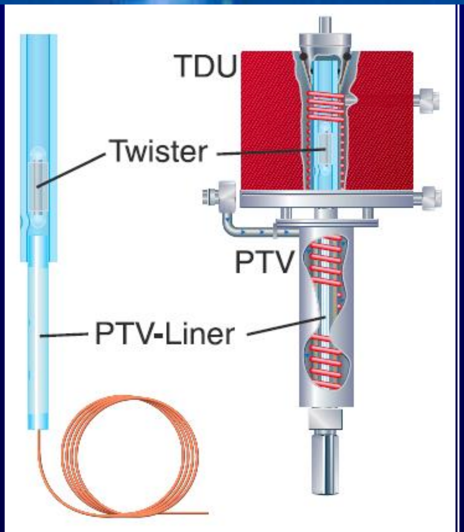
Klesk, K.; Qian, M. *J. Agric. Food Chem.* **2003**, 51*,* 3436-3441
Klesk, K.; Qian, M. *J. Food Sci.* **2003**, *68*, 697-700.

Impact of Agronomic Conditions

- Variation year to year
  - Michael Qian and Yuanyuan Wang. *J. Food Sci.* **2005,** 70(1):13-20
- Variations at different location
  - Wang, Yuanyuan; Finn, Chad; Qian, Michael C. *J. Agric. Food Chem.* **2005,** 53, 3563-3571
- Variation among the genotypes is the greatest

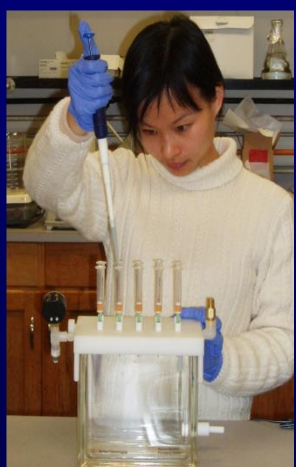
Volatile Quantification with Stir Bar Sorptive Extraction (SBSE)



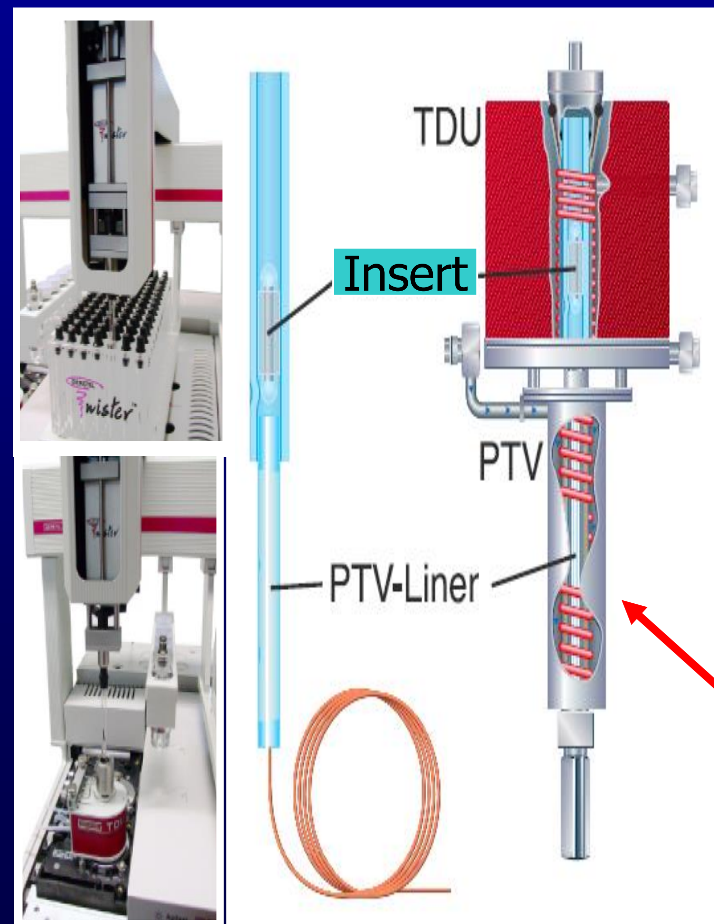


Furaneol Analysis with LiChrolut-EN SPE and Microvial Inert Thermal Desorption

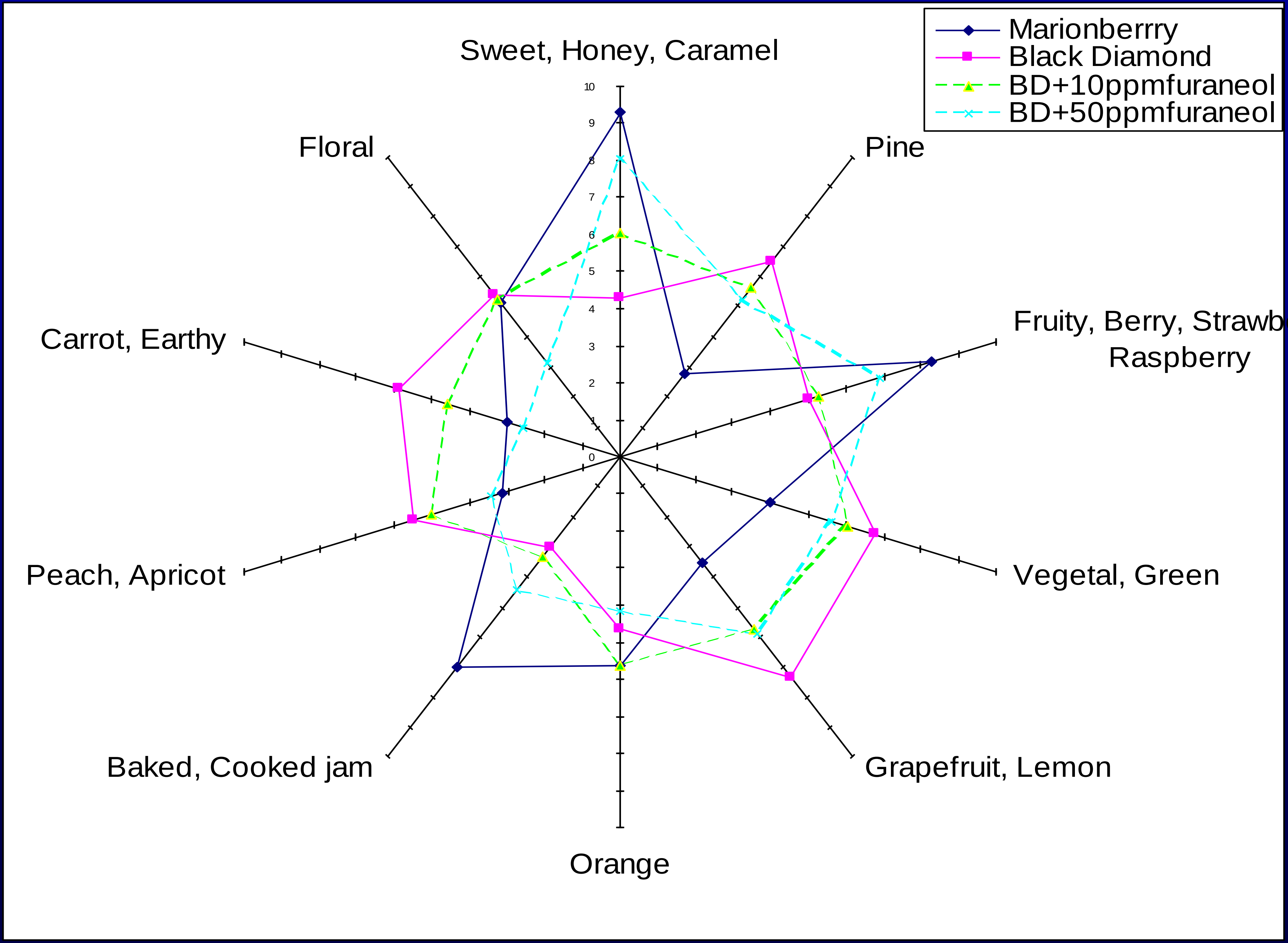
30 mL of juice was passed through the SPE, 200mg



1. Rinsed with water
2. Eluted with EtOAc
3. Conc. to ~500µL with N_2
4. 20µL placed into micro insert

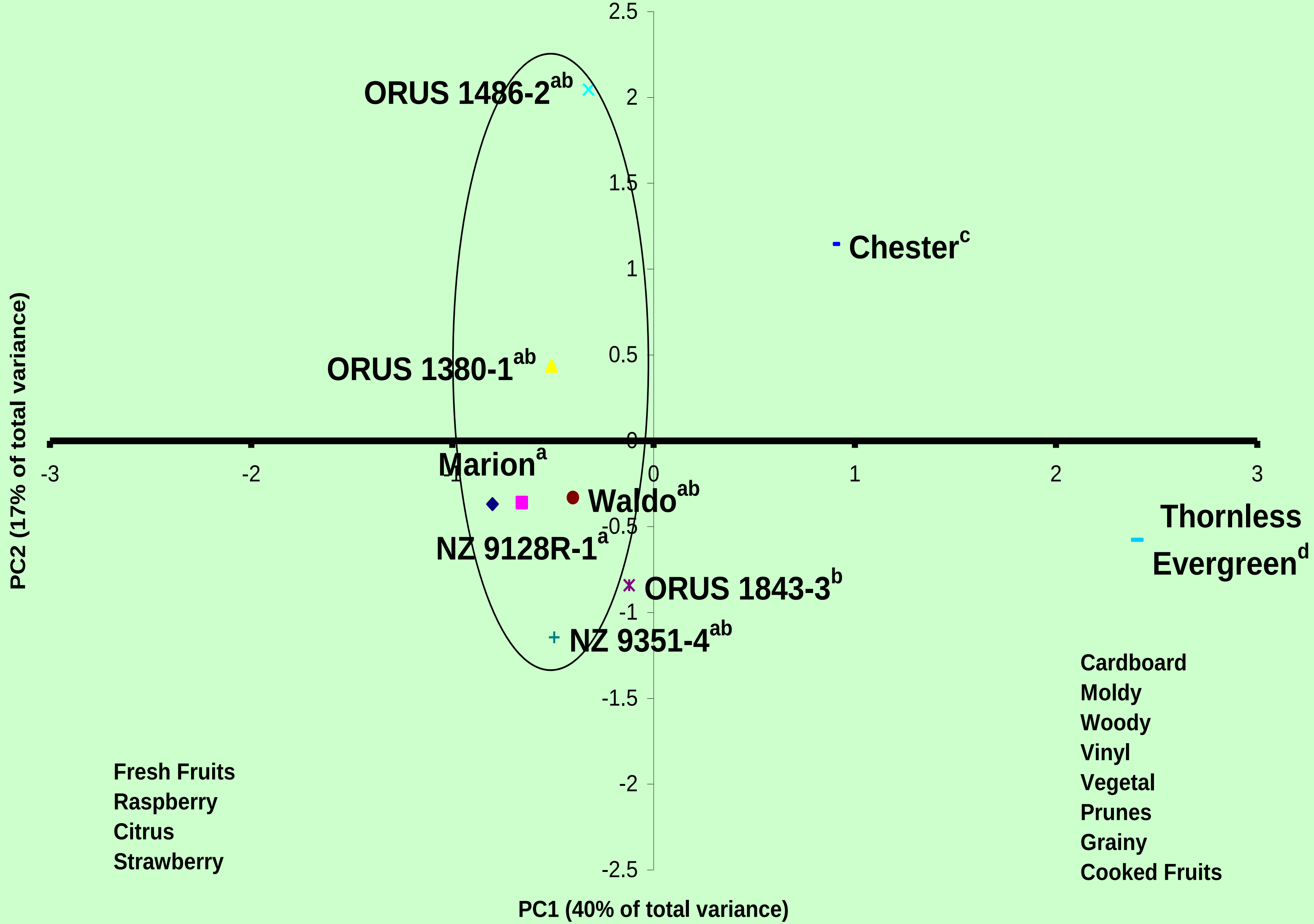


CIS 4 PTV, packed with 1 cm of Tenax



Marionberrry
Black Diamond
BD+10ppmfuraneol
BD+50ppmfuraneol
Sweet, Honey, Caramel
Pine
Fruity, Berry, Strawbe
Raspberry
Vegetal, Green
Grapefruit, Lemon
Orange
Baked, Cooked jam
Peach, Apricot
Carrot, Earthy
Floral
10
9
8
7
6
5
4
3
2
1
0

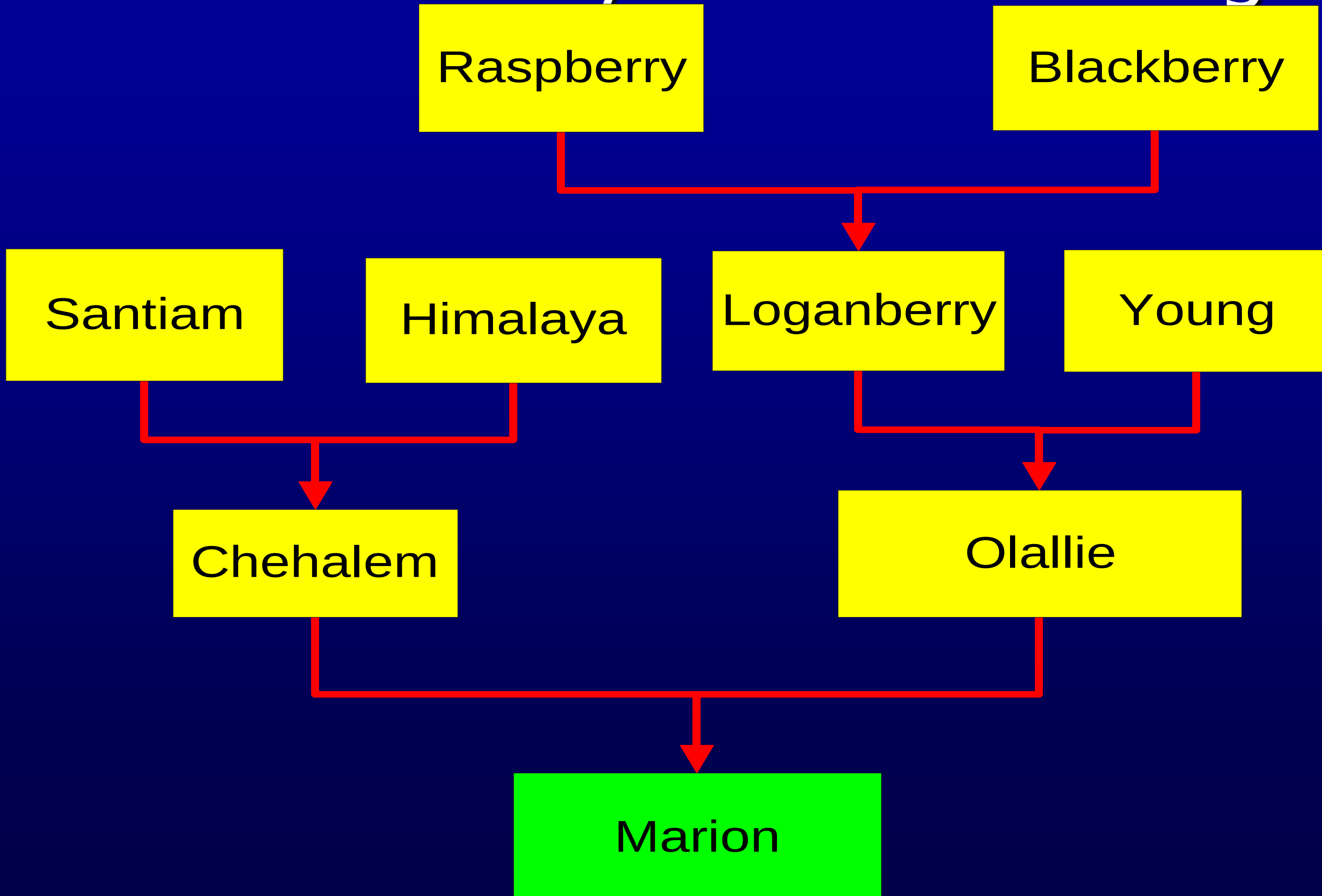
Sample positioning in aroma space (PC1 vs. PC2)
[PC1 sample effect P<0.001; samples with different superscript letters on PC1 are significantly different from one another (Tukey's P<0.05)]



Furaneol in Blackberry Samples

Blackberries	Names	Con. (mg/kg)
03-9128-1	Black Diamond	0.63
03-1369-3	Obsidian	2.49
03-1452-1	Metolius	0.64
03-1486-2	Nightfall	0.44
04-1380-1	Black Pearl	2.50
04-Marion	Marion	4.22
04-Waldo	Waldo	4.97

Aroma Inheritability in 'Marion' Pedigree



Aroma inheribility (β-Ionone) in 'Marion' Pedigree to assist the development of new blackberry cultivar

Raspberry (300 ppb) × Blackberry → Logan (90 ppb)

Santiam (0.3 ppb) × Himalaya (ND) → Chehalem (ND)

Logan (90 ppb) × Young → Olallie (50 ppb)

Chehalem (ND) × Olallie (50 ppb) → Marion (4 ppb)

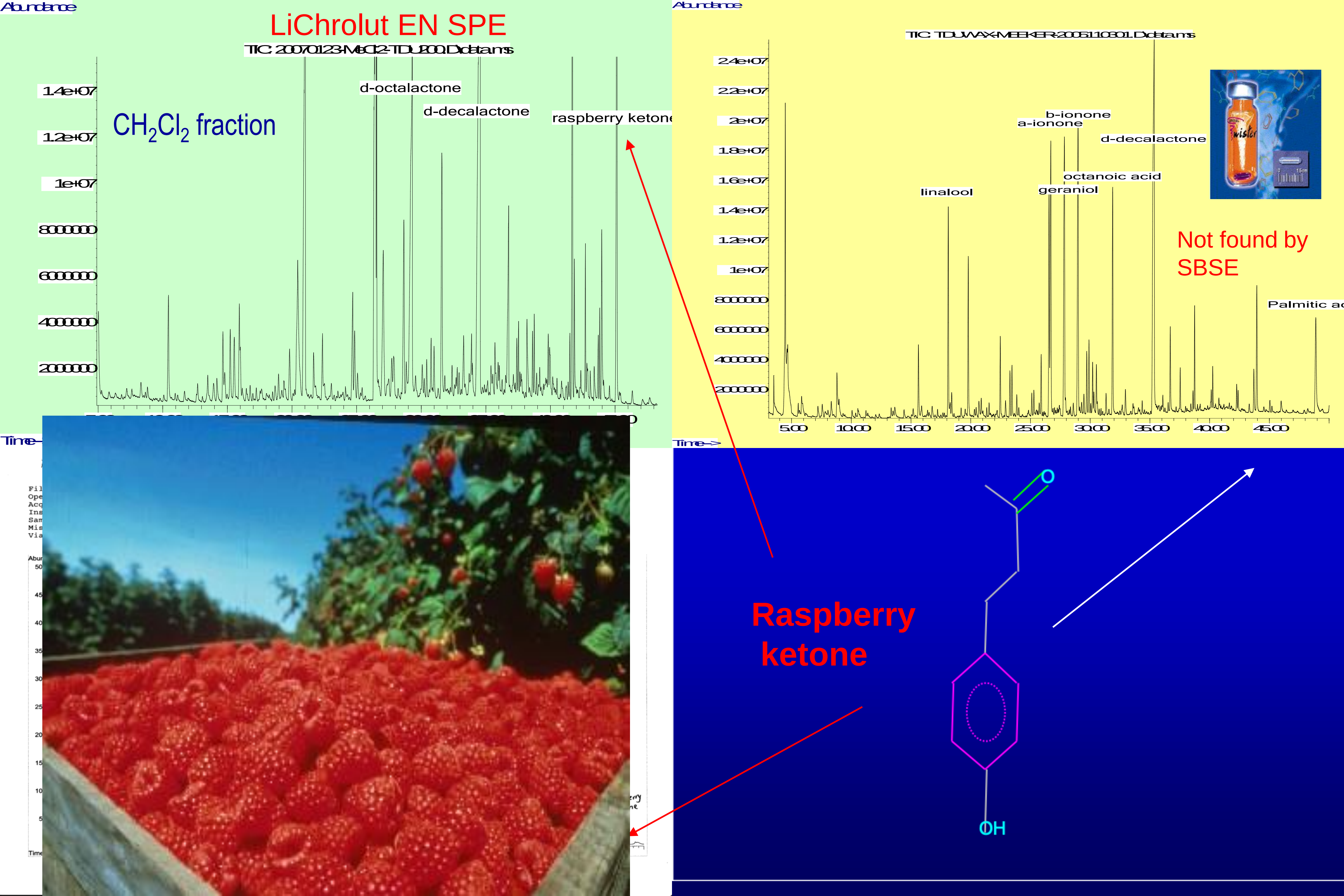
•Du et al. J. Agric. Food Chem. 2010, 58 (6), 3694-3699

Good Flavor Thornless Blackberries Released by USDA Breeding Program

Obsidian (1369-3)
Metolius (1452-1)
Nightfall (1486-2)
Black Pearl (1380-1)
Black Diamond

Raspberry Bushy Dwarf Virus (RBDV) Resistant Raspberry

- Transgenic raspberry resist to RBDV


LiChrolut EN SPE
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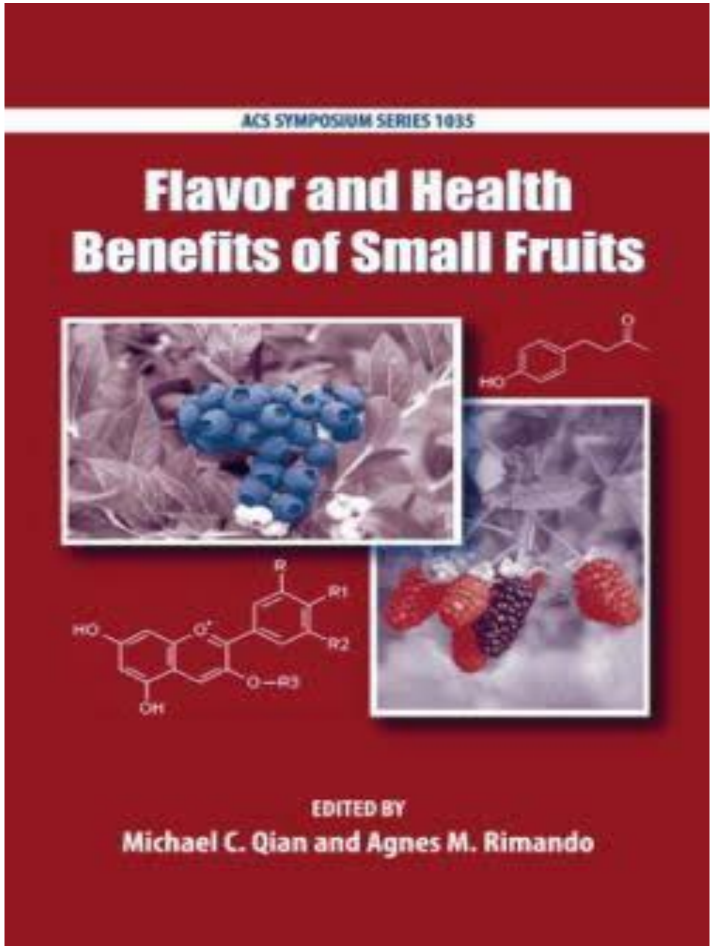
Abundance
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
CH_2Cl_2 fraction
d-octalactone
d-decalactone
raspberry ketone
Time-->
TIC: TDU-WAX-MEEKER-20051103-01.D\data.ms
Abundance
2.4e+07
2.2e+07
2e+07
1.8e+07
1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
b-ionone
a-ionone
d-decalactone
octanoic acid
geraniol
linalool
Not found by SBSE
Palmitic ac
500
1000
1500
2000
2500
3000
3500
4000
4500
Time-->
Raspberry ketone
O
OH

Michael Qian and Agnes Rimando. Flavor and Health Benefits of Small Fruits – ACS symposium, Philadelphia- Aug. 17-21, 2008

Co-editor with Agnes Rimando in 2010



Michael Qian and Agnes Rimando. Environmental effect on volatile and nonvolatile compounds– The 250 American Chemical Society National Meeting, Aug. 15-20, 2015, Boston, MA

Environmental Effect on Plant Volatile Formation & Nonvolatile Composition Section C

Boston Conv/Exhibit Ctr Rm 209 M. C. Qian, A. M. Rimando, *Organizers, Presiding*

8:25 Introductory Remarks.

8:30 284. Impact of water deficit on volatile composition of grapes and wine. **M.C. Qian**, K. Sh

8:55 285. Influence of sunlight exposure on Pinot noir grape and wine volatile composition. M.C. Qian, **F. Yuan**

9:20 286. Not your ordinary *terroir* - the role of pathogenesis related proteins (PRPs) in limiting tannin extraction across winegrape varieties and regions. L.F. Springer, **G.L. Sacks**

9:45 Intermission.

10:00 287. Accumulation of exogenous volatiles in *Vitis vinifera* fruit and leaves as nonvolatile glycoconjugates. **K. Wilkinson**, R. Ristic, J. Culbert, L. Van der Hulst, A. Pardo-Garcia, G. Alonso, R. Salinas, N. Lloyd, Y. Hayasaka

10:25 288. Changes in orange juice flavor volatile and non-volatile compounds in response to citrus greening or Huanglongbing (HLB) disease and disease management strategies. **B. Elizabeth**, A. Plotto, J. Bai, J.A. Manthey, S. Raithore, H. Yang, S. Deterre, S. Dea

10:50 289. Postharvest practices to alleviate flavor loss of tomatoes under current marketing systems. **J. Bai**, B. Elizabeth, A. Plotto, L. Wang

11:15 290. Molecular assessment of metabolome changes in carrots (*Daucus carota* L.) induced by abiotic stress challenges. **C. Dawid**, A. Dunkel, T. Nothnagel, D. Ulrich, B. Singldinger, D. Günzkofer, T. Hofmann

Blueberry-Dr. Rimando's Favorite Fruit

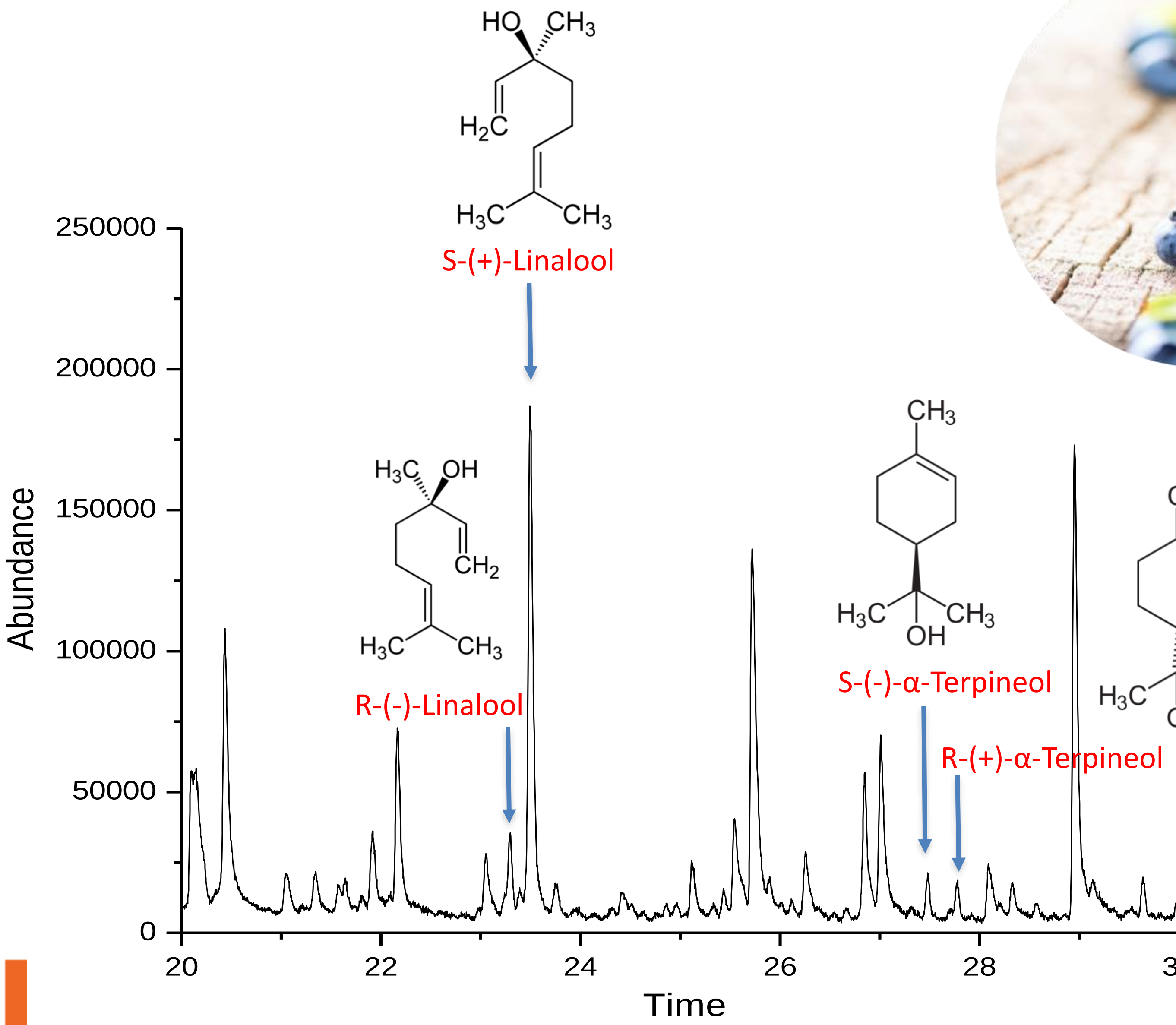
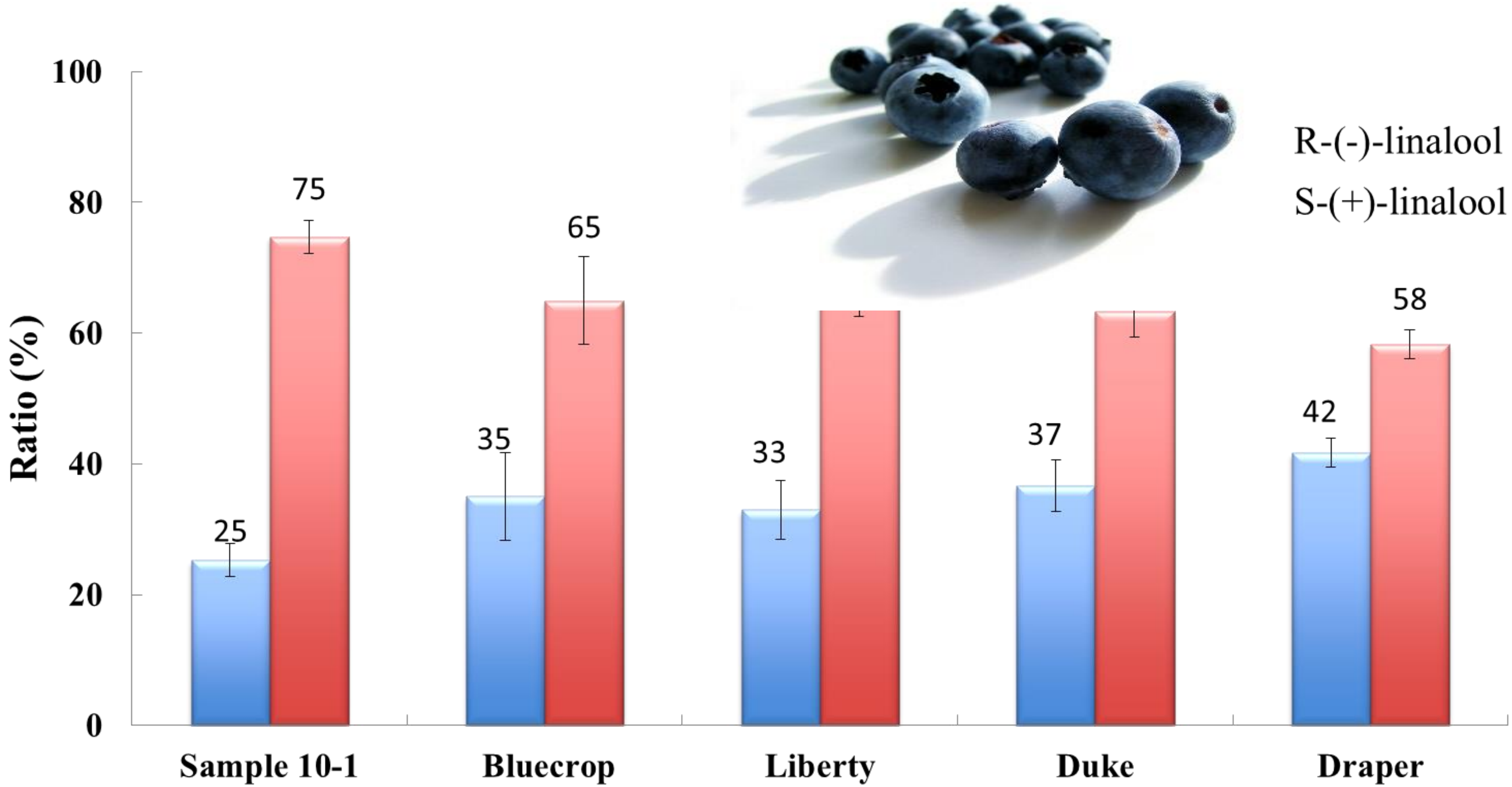


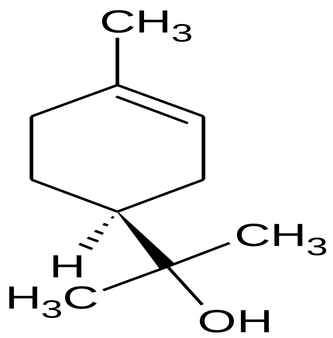
Fig. GC-MS/O spectrogram of ‘Bluecrop’ blueberry enantiomers

Oregon State
UNIVERSITY

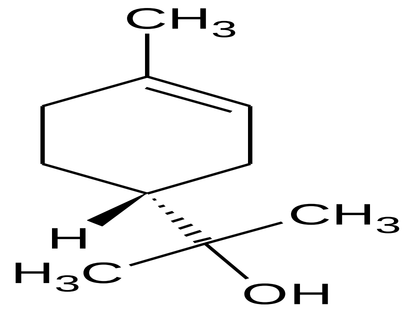
nantiomeric form of Linalool in Blueberry



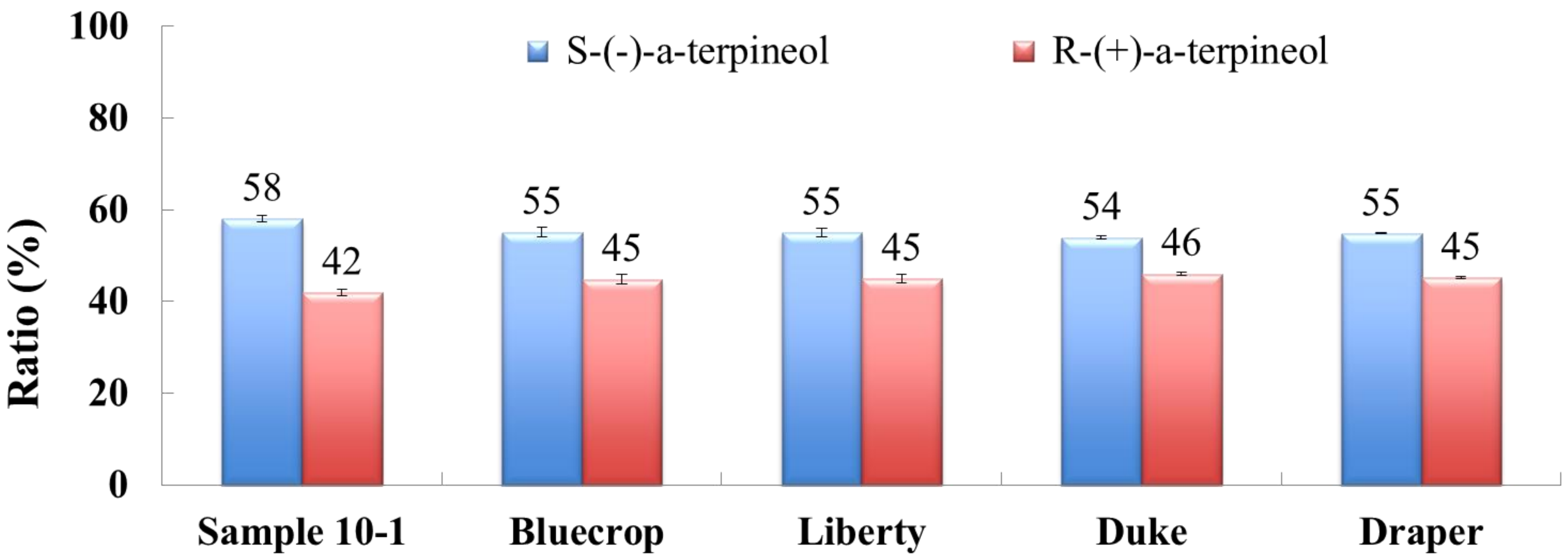
Enantiomeric compounds



(S)-(-)-alpha-terpineol
coniferous odor character

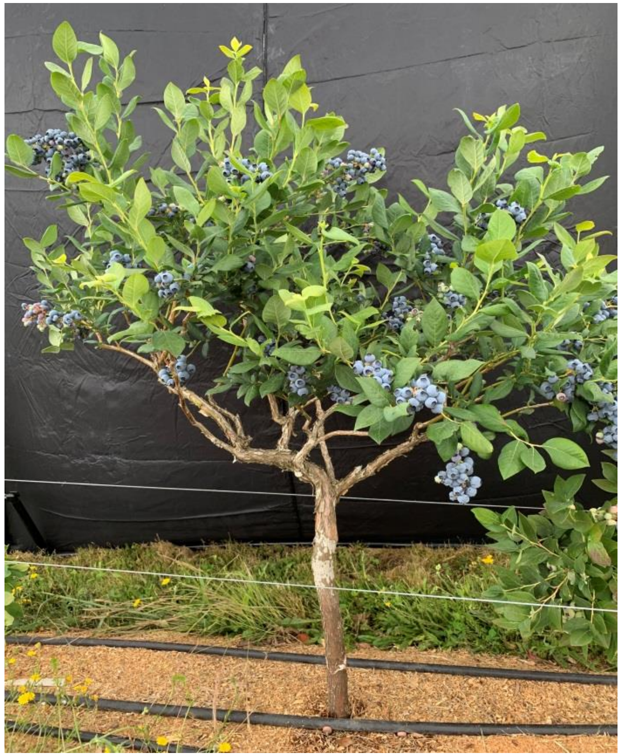


(R)-(+)-alpha-terpineol
heavy floral typically lilac odor



Bluebery Mechanization

Tree Blueberry for Machine Harvest



CLOSING REMARKS

It was ACS that brought Agnes and me together about 20 years ago. Over the years our professional relationship grew closer as she followed me in the AGFD chair role, we received distinguished service awards together, became ACS fellows together, and so on. Our collegial relationship quickly grew into much more as we found ourselves arranging time to share our international adventures, our love of Asian food, and our lives in general, with each other during ACS and other national meetings too. We met at her home in Mississippi and she had planned to visit mine in Chicago. I greatly miss Agnes and will always remember her with the greatest esteem and affection.

Remarking on any life, particularly once such Agnes's, is always a tall order,. Though I knew it would be incomplete, I offered this remembrance of her for ACS last December.

JAFC article SLIDE

It echoes her legacy of scientific, leadership, and mentorship contributions that you've already heard about from others today. Thank you to all our speakers and to my co-organizers for doing such a nice job bringing to life this celebration of Agnes.

Here, I'd like to focus *beyond* the professional, and more on the personal especially for those of you who may not have had the opportunity to know Agnes or work with her as I did.

Agnes' brother Philip remarked that in this picture she appeared as an angel to their family. Angels are usually depicted as benevolent celestial beings of extraordinary physical beauty.

BEAUTY PAGENT SLIDE

Here she is at 9 years old, in her native Philippines, looking anything but the budding scientist. Already beautiful. Characteristic of her humility, Agnes never mentioned this beauty pageant to me. Though proud of her many meaningful achievements, she never boasted.
She was also a person of great kindness, regularly bringing me thoughtful treats – dried mangoes from the Philippines, a purse hanger she felt I needed to safeguard my valuables in the many restaurants we explored together, or urging me to add blueberries to my daily diet.

One of her most appreciated traits surfaced when she was faced with the most contentious of professional issues, or any sticky situation, really. Agnes was always ready to give the benefit of the doubt. "I think it's all just been a big misunderstanding" she would say. Her equanimity and forgiving spirit made her easy to work with and be with. Yes, Agnes was beautiful – both outside and inside.

It is said that angels are attracted by the sound of laughter. With Agnes, laughter abounded.

LAUGHING WITH NIECES & NEPHEWS SLIDE

She was quick to laugh and slow to show any temper. Instead, she always found the humor in life. No topic was off limits. As I recall, the last peals of laughter we shared covered the most discomforting indignities we endured during annual female health exams! It was always easy to bridge the professional with the personal Agnes. That and her endearing smile and laughter may be what I miss most.

ANGELIC ADULT AGNES SLIDE

English writer, poet, philosopher and theologian G.K. Chesterton once wrote
“perhaps angels can fly because they take themselves so lightly!”

Agnes certainly flew through her own life, and the lives of many others. I like to imagine she has just flown off to be an angel elsewhere.

Thank you.

Jane Leland
August, 2019