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Thursday, September 18, 2014

“Tragic Chemical Accidents: Combustible Dust Hazards”

Dr. Tara Henriksen, Senior Chemical Engineer and Certified Fire and Explosion Investigator, CASE Forensics Corp.



Thursday, September 25, 2014

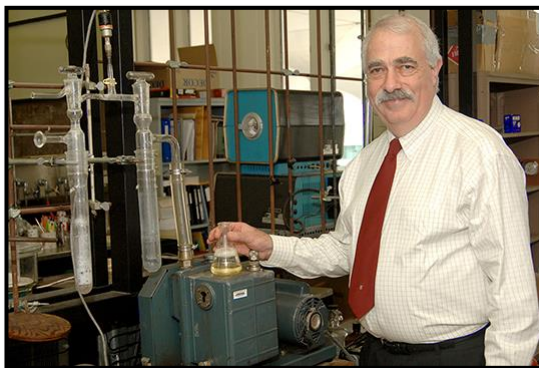
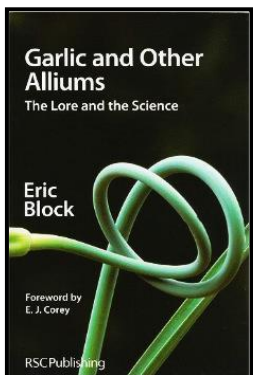
“Pharmacoeconomics and IP Strategies in Drug Development” Session 7

Dr. Richard Willke, Health Economist, Pfizer
Dr. Robert Koch, Partner and IP Specialist, Milbank

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Thursday, November 13, 2014



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“Garlic and Other Alliums: The Lore and the Science”

Co-produced with the ACS Fellows Program



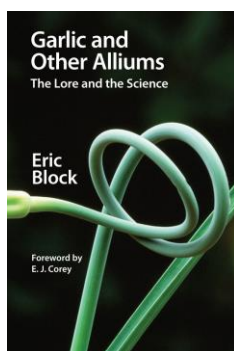
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Garlic and Other Alliums: The Lore and the Science



Dr. Eric Block
*Department of Chemistry, University at Albany, SUNY
Albany, New York
September 11, 2014*

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Allium: Topics Covered

- Allium botany
- Allium origin
- Allium in the arts
- Allium cultivation & sale
- Allium pesticides & repellents
- Allium health benefits
- Allium chemistry



Garlic's Cousins: The Genus *Allium*

<i>A. Ascalonicum</i>	Shallot
<i>A. Cepa</i>	Onion
<i>A. Giganteum</i>	Giant Flowering Onion
<i>A. Moly</i>	Lily Leek
<i>A. Porrum</i>	Leek
<i>A. Sativum</i>	Garlic
<i>A. Schoenoprasum</i>	Chives
<i>A. Tricoccum</i>	Ramp

The genus *Allium* includes a total of 600-750 species

The Diversity of Garlic Cultivars



Ajo Rojo (Creole)



German Giant (Rocambole)



Thermadrome (Asiatic)



Italian Purple (Artichoke)



Purple Glazer (Glazed Purple Stripe)



Slovenian (Rocambole)

Source: www.gourmetgarlicgardens.com/variety

Ornamental Alliums: A Feast for the Eyes



Audience Survey Question

Where in the world did garlic and onion originate?

- Pompeii
- Egypt
- Russian Asia
- Africa
- Japan

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Eduard August von Regel

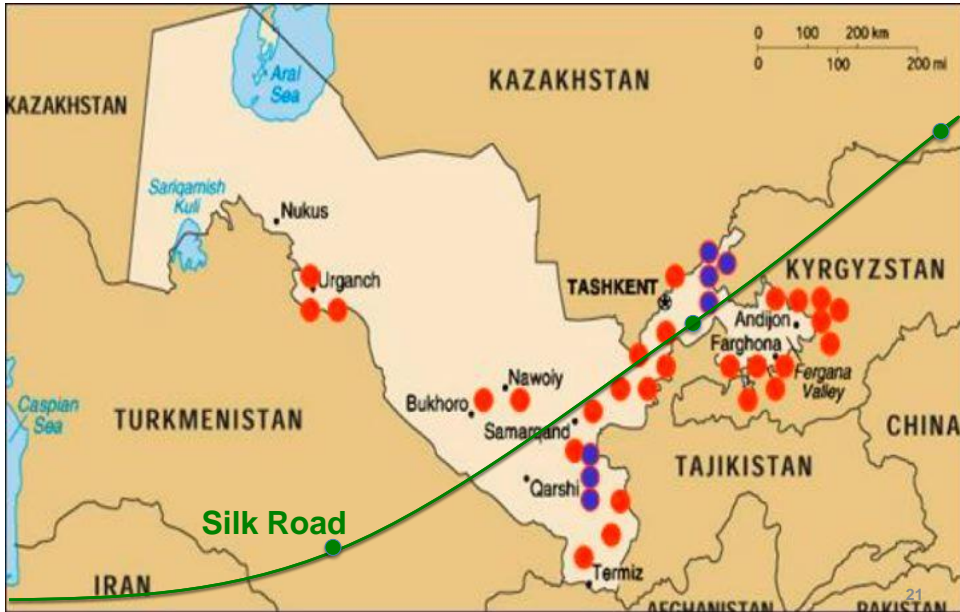
(1815–1892): Director of Russian Imperial Botanical Garden of St. Petersburg. Directed biological collections around the world; described & named numerous alliums



Allium alexeianum Regel, *Allium altissimum* Regel, *Allium andicolum* Regel, *Allium backhousianum* Regel, *Allium bakeri* Regel, *Allium bodeanum* Regel, *Allium boissieri* Regel, *Allium borschaowii* Regel, *Allium bucharicum* Regel, *Allium caricoides* Regel, *Allium caricoides* Regel, *Allium darwasicum* Regel, *Allium derderanum* Regel, *Allium derderianum* Regel, *Allium djmilense* Boiss. ex Regel, *Allium dolonkarense* Regel, *Allium drummondii* Regel, *Allium elatum* Regel, *Allium fetisowii* Regel, *Allium fibrosum* Regel 1887, *Allium filidens* Regel, *Allium filifolium* Regel, *Allium giganteum* Regel, *Allium gusaricum* Regel, *Allium herderianum* Regel, *Allium hoeltzeri* Regel, *Allium jacquemontii* Regel, *Allium karataviense* Regel, *Allium kaschianum* Regel, *Allium kaufmannii* Regel, *Allium kokanicum* Regel, *Allium longicuspis* Regel, *Allium longiradiatum* Regel, *Allium macrorhizon* Regel, *Allium maximowiczii* Regel, *Allium megalobulbon* Regel, *Allium oreophiloides* Regel, *Allium ostrowskianum* Regel, *Allium oviflorum* Regel, *Allium platystylum* Regel, *Allium renardii* Regel, *Allium sewerzowii* Regel, *Allium stipitatum* Regel, *Allium stoliczki* Regel, *Allium suworowii* Regel, *Allium szovitsii* Regel, *Allium talassicum* Regel

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Center of Origin of Garlic is “Russian Asia,” explored by Regel’s son and his team



Readying plant specimens for transport from Russian Asia.

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Transporting plant specimens from Russian Asia.

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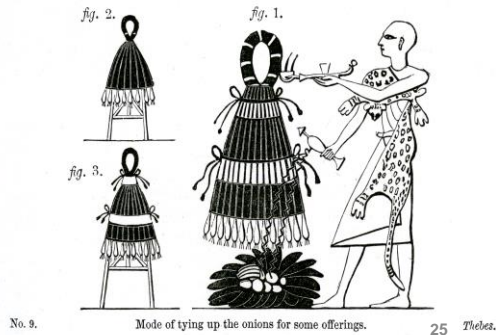
What is known about the role of garlic and other alliums in the *arts and literature*?

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Alliums in Ancient Egypt



Sprig of garlic buried with Nakhtefmut, 900 BC, Thebes, Egypt



No. 9. Mode of tying up the onions for some offerings. 25 Thebes.



Historia Naturalis Pliny the Elder (77 CE)

Garlic has powerful properties, and is of great benefit against changes of water and of residence. **It keeps off serpents and scorpions by its smell ...** It cures bites when drunk or eaten, or applied as ointment ... it is an antidote against the poisonous bite of the shrew-mouse ... pounded garlic has been given in milk to asthmatics ... The ancients used also to give it raw to madmen.

1480 Venetian edition: Collection of Oxford University Bodleian Library

Count Dracula and Garlic



“The Professor’s actions were certainly odd and not to be found in any pharmacopeia that I ever heard of. First he fastened up the windows and latched them securely. Next, taking a handful of the [garlic] flowers, he rubbed them all over the sashes, as though to ensure that every whiff of air that might get in would be laden with the garlic smell.

Then with the wisp he rubbed all over the jamb of the door, above, below, and at each side, and round the fireplace in the same way. It all seemed grotesque to me, and presently I said, ‘Well, Professor, I know you always have a reason for what you do, but this certainly puzzles me. It is well we have no skeptic here, or he would say that you were working some spell to keep out an evil spirit.’ I could see that the Professor had carried out in this room, as in the other, his purpose of using the garlic. The whole of the window sashes reeked with it, and round Lucy’s neck, over the silk handkerchief which Van Helsing made her keep on, was a rough chaplet of the same odorous flowers.” **Bram Stoker, *Dracula* (1897)**

27

See: Liisa Ladouceur, *How to Kill a Vampire: Fangs in Folklore, Film and Fiction*, ECW Press, Toronto, 2013

Shakespeare on Alliums



***Antony and Cleopatra*, Act 1, Scene 2**

Indeed the tears live in an onion that should water this sorrow.

***A Midsummer Night's Dream*, Act 4, Scene 2**

And, most dear actors, eat no onions nor garlic for we are to utter sweet breath; and I do not doubt but to hear them say, it is a sweet comedy

***Henry V* Act 4, Scene 7**

Your majesty says very true: if your majesties is remembered of it, the Welshmen did good service in a garden where leeks did grow, wearing leeks in their Monmouth caps; which, your majesty know, to this hour is an honourable badge of the service; and I do believe your majesty takes no scorn to wear the leek upon Saint Davy's day.

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Onions in Painting: Vincent van Gogh



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Alliums in Stamps and in the Bible

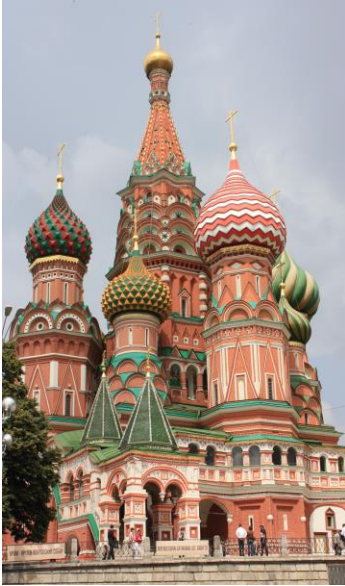


“We remember the fish which we did eat in Egypt, the cucumbers, the melons, leeks, onions and garlic.”

Numbers 11:4-6

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Onion Domes in Architecture: Saint Basil's Cathedral, Moscow



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Garlic Domes in Architecture: Casa Batlló, Antoni Gaudí, Barcelona



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What do we know about the *cultivation and sale* of garlic and onions?

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Audience Survey Question

Which country is the world's largest producer of garlic?

- Egypt
- China
- USA
- Liechtenstein
- Japan

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800,000 Acres of Garlic: Shandong, China



35



China Garlic Production: 20 mtons (2012)

China Onion Production: 23 mtons (2012)

U.S. Garlic Production: 0.2 mtons (2012)

U.S. Onion Production: 3.3 mtons (2012)

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Cairo Garlic Market



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Cairo Garlic Market

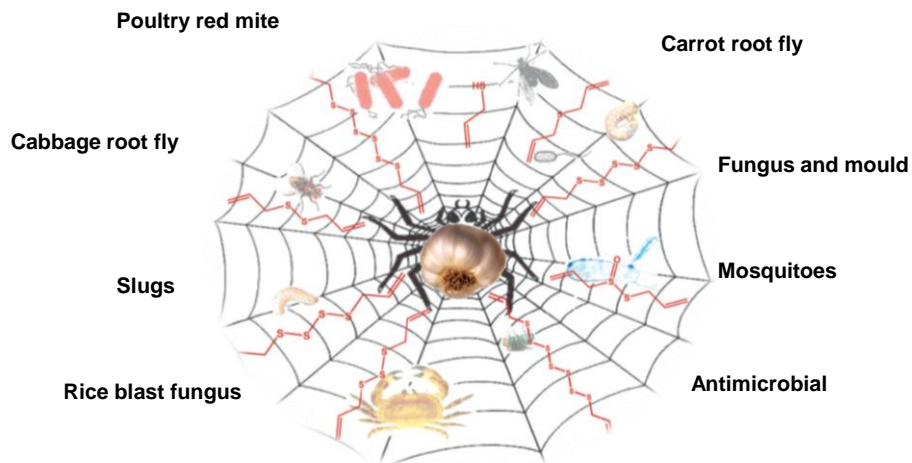


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What do we know about the use of garlic as a *pesticide*?

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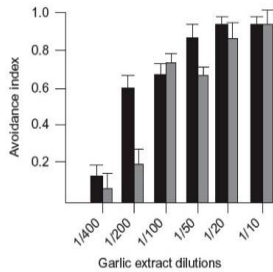
Targets for Garlic Sulfur Compounds



Münchberg, Anwar, Mecklenburg, Jacob, Polysulfides as biologically active ingredients of garlic. *Org. Biomol. Chem.* 2007, 5 (10), 1505-18

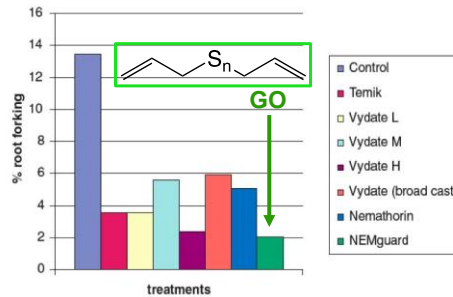
40

Garlic Oil as a Green Nematicide



Far left: carrots showing multiple root nematode damage. **Mid left:** avoidance index of two populations of nematode *C. elegans* tested with a single drop of garlic oil at different dilutions (*Embo J* 2004, 23, 1101)

Right: carrot crop field trial comparing nematicidal effect (%reduction of root forking) of a garlic-oil (GO) based material, **NEMguard**, with commercial nematicides **Temik**, **Vydate** and **Nemathorin** at comparable application levels.



Ecospray: UK company sells garlic oil-based, environmentally benign pesticides www.ecospray.com

Ecospray About Us | Products | Technology | Regulation | News | Contact

Science inspired by nature

Products Research Global distribution What we do

Annex 1 listing, EU directive 91/414; UK PSD approved

What do we know about the *health benefits* of garlic?

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ANGEWANDTE CHEMIE

A Journal of the Gesellschaft Deutscher Chemiker

International Edition in English

31/9 1992

Reviews: Polyynes and Fullerenes · Chemistry of Garlic and Onion: Conformational Design
 Highlights: $[Pt^0]$ as Ligand · Asymmetric Syntheses · Inorganic Host-Guest Compounds

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Supposed Health Benefits of Garlic:

Antibiotic, anticancer, antithrombotic, antioxidant, cholesterol-triglyceride lowering, blood pressure lowering

4470 (>1963) publications on garlic

PubMed: Results by year

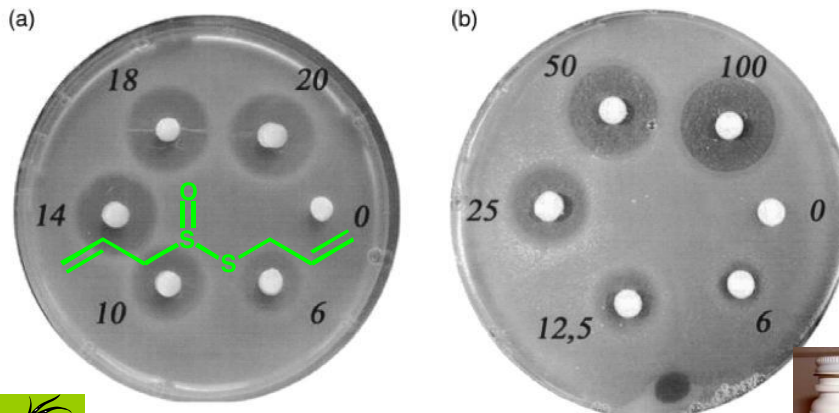


Garlic Health Supplements

US sales (2004)
\$150,200,000



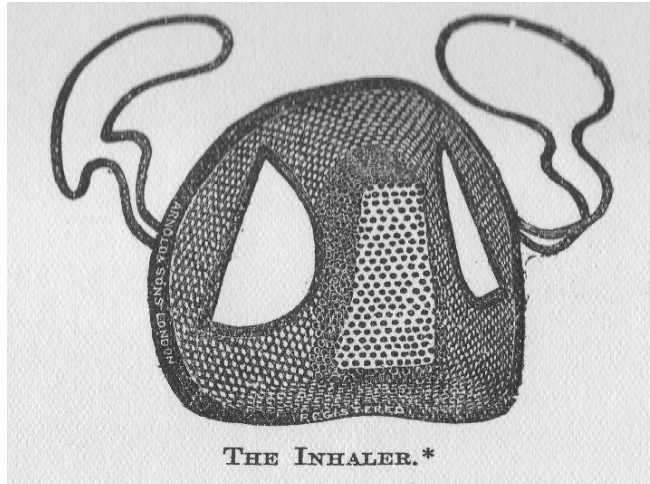
E. coli-seeded Petri Plate Assays Comparing Antimicrobial Activity of (a) Garlic Extract (0-20 μ L of 280 μ g Alicin in 20 μ L)(left) and (b) Ampicillin (0-100 μ g)(right)



Slusarenko et al. Alicin: Chem. & Biol. Prop. Physiol. Mol. Plant Pathol. 2004, 65, 79-89; Molecules 2014, 19, 12591-12618



Face Mask for Inhalation of Garlic Oil for Treatment of Tuberculosis



W.C. Minchin, *A Study in Tubercle Virus*, London, 1927

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Garlic Treatment: Burns to Feet and Elbow (Don't try this at home!)

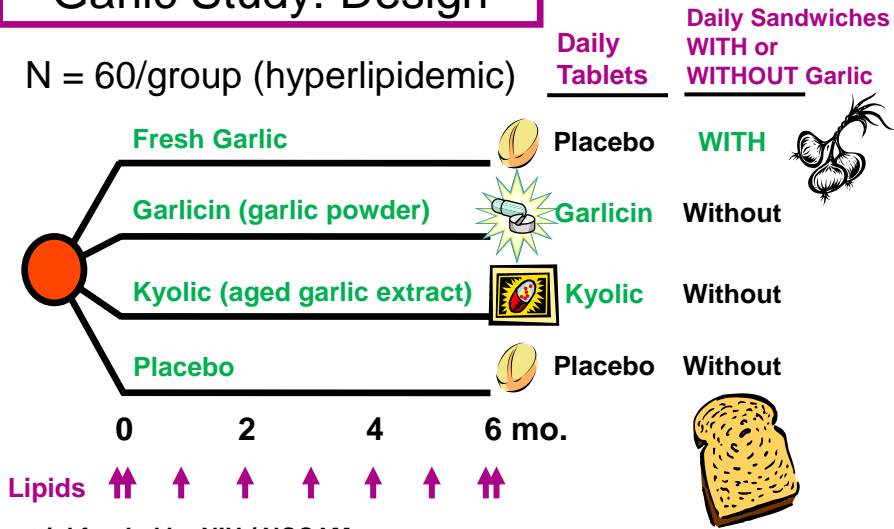


“Garlic Burns.” *Burns* 2001, 27, 781-782; 2004, 30, 612-613; 2009, 35, 300-302

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Does Garlic Reduce Cholesterol Levels?

Garlic Study: Design



3-Year trial funded by NIH / NCCAM

Stanford Center for Research in Disease Prevention: C.D. Gardner, L. Lawson, E. Block

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The Effect of Raw Garlic vs. Commercial Garlic Supplements on Plasma Lipids in Moderately Hyper-cholesterolemic Adults: A Randomized Clinical Trial

C.D. Gardner, L.D. Lawson, E. Block, L. M. Chatterjee, A. Kiazand, R.R. Balise, H.C. Kraemer



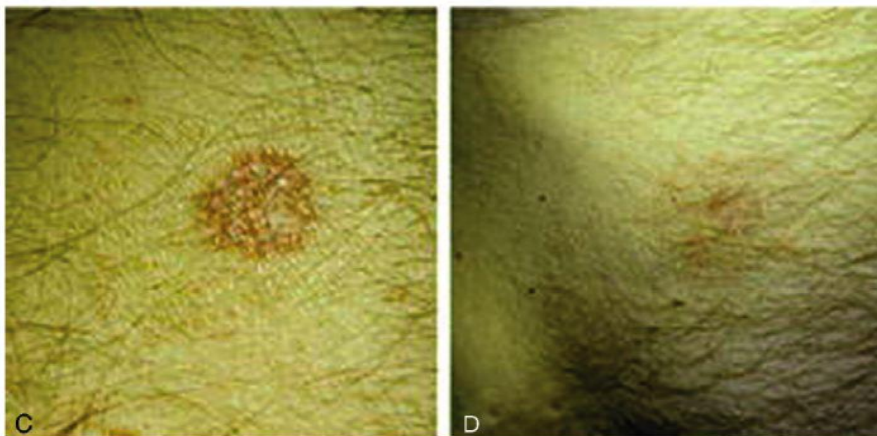
Archives of Internal Medicine,
2007, 167, 346



CONCLUSIONS – None of the forms of garlic used in this study, including raw garlic, when given at doses of roughly a 4-gram clove/day 6 days/week for 6 months, had statistically or clinically significant effects on LDL-C or other plasma lipid concentrations among moderately hypercholesterolemic adults.

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Effect of **Ajoene** on Basal Cell Carcinoma Tumor before (C) and 6 Months after (D) Topical Application. The Respective Tumor Surface Areas are C, 195 mm² and D, 24 mm²



Arch. Dermatol. Res. **2003**, *295*, 117-123; also see *Mol. Cells* **2014**, *37*, 547-553:
“Systemic Approaches Identify a Garlic-Derived Chemical, Z-ajoene, as a
Glioblastoma Multiforme Cancer Stem Cell-Specific Targeting Agent” ⁵¹

What is known about the
organosulfur chemistry of
garlic and onion or “Allium
chemistry”?

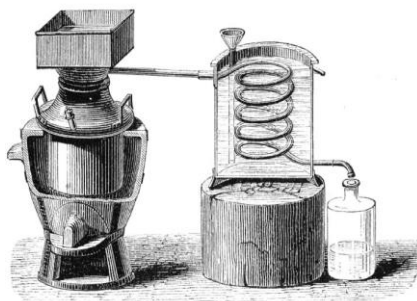
Audience Survey Question

What chemical species is named after garlic?

- allyl
- gallium
- stinkium
- aluminium
- garlicium chloride

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Early Allium Chemistry



An alembic of the type used to distil garlic oil

1844: Wertheim distills garlic and isolates garlic oil, “allylschwefel” = “allyl sulfur”, the origin of the name “allyl” (from *Allium*)

1856: Hofmann synthesizes diallyl sulfide, having a “strong smell of garlic”, and allyl alcohol

1891: Semmler finds that garlic oil is in fact a mixture of diallyl disulfide and trisulfide

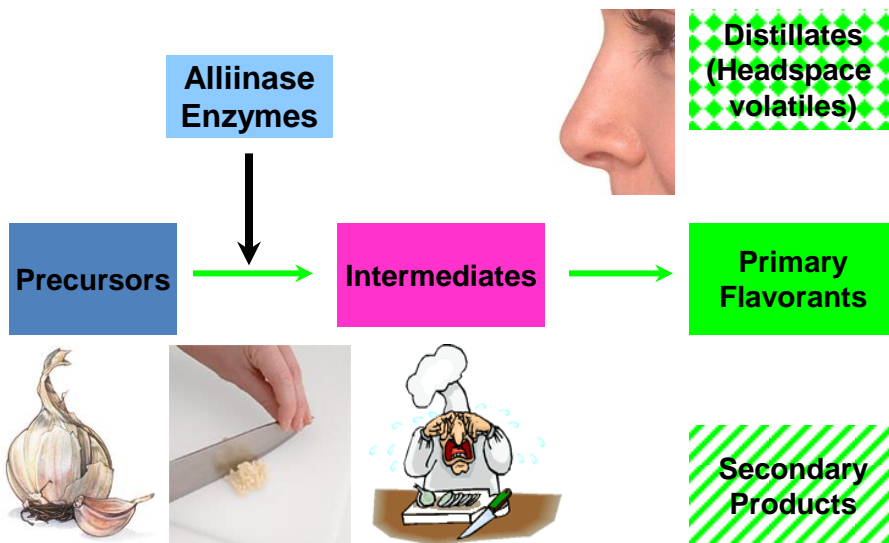


August Wilhelm von Hofmann, Director of the Royal College of Chemistry of London, and founder of the German Chemical Society



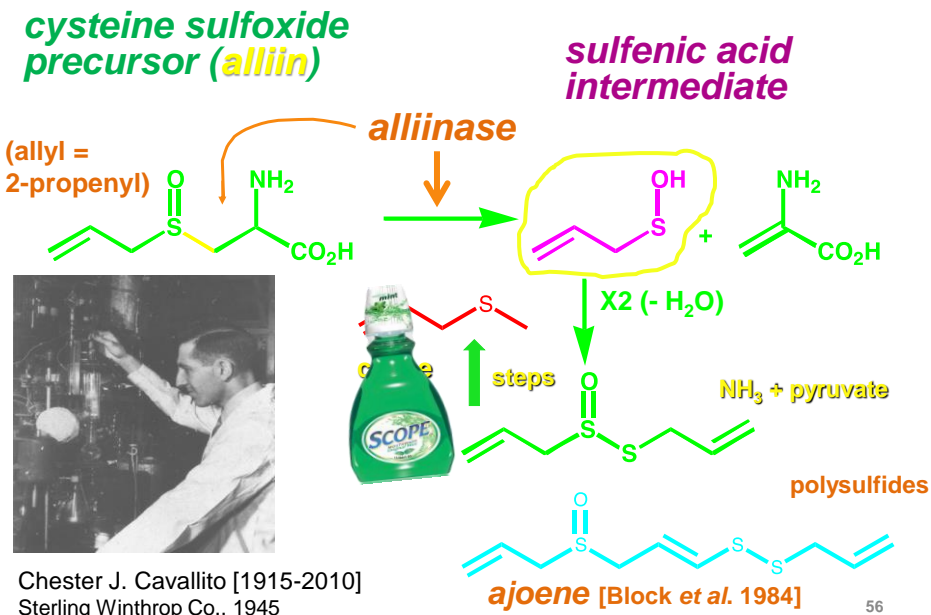
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Allium Chemistry



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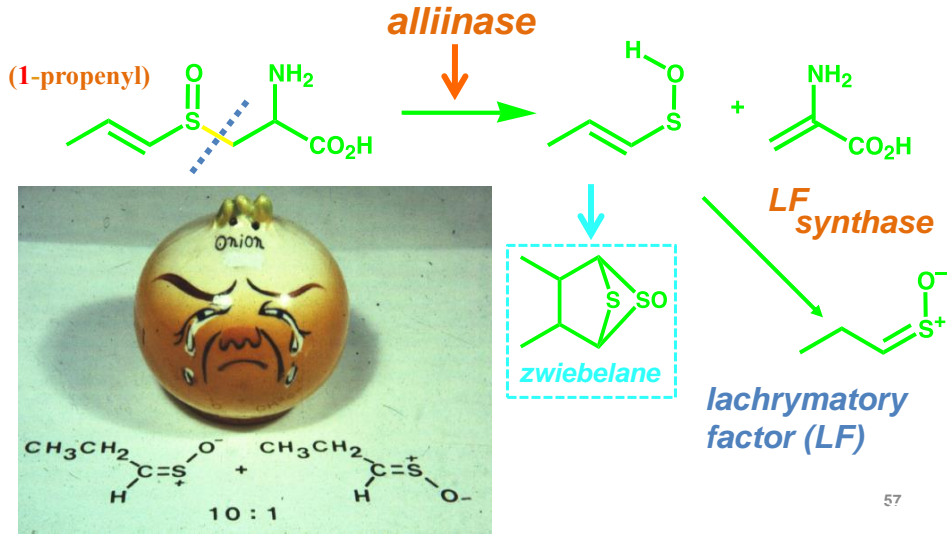
Garlic Chemistry



Onion Chemistry

cysteine sulfoxide precursor (isoalliin)

sulfenic acid intermediate



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DART MS

DART (Direct Analysis in Real Time) mass

spectrometry allows high resolution measurement of mass spectra of plant samples at ambient atmospheric conditions with no sample preparation.



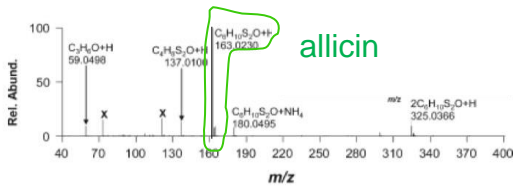
Audience Survey Question

What is elephant garlic?

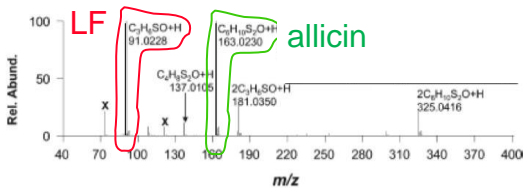
- garlic with a long memory
- not a garlic but a leek which can make you cry
- garlic with tusks
- not a garlic but a stinky relative of an artichoke
- odorless garlic

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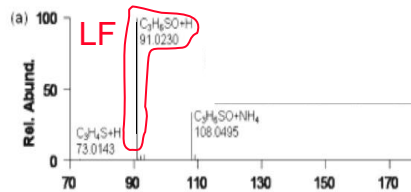
Elephant Garlic (*A. ampeloprasum*) but not Garlic Produces LF as well as Allicin



PI-DART mass spectrum of **garlic**
(allicin + H⁺ = 163.0263)



PI-DART mass spectrum of **elephant garlic**
(LF + H⁺ = 91.0235; LF + NH₄⁺ = 108.0506;
allicin + H⁺ = 163.0319)



PI-DART mass spectrum of **onion**
(LF + H⁺ = 91.0230; LF + NH₄⁺ = 108.0506)

Block, Dane, Thomas, Cody, *J. Agric. Food Chem.* **2010**, *58*, 4617

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Allium siculum (Nectaroscordum siculum) used as a seasoning in Bulgaria



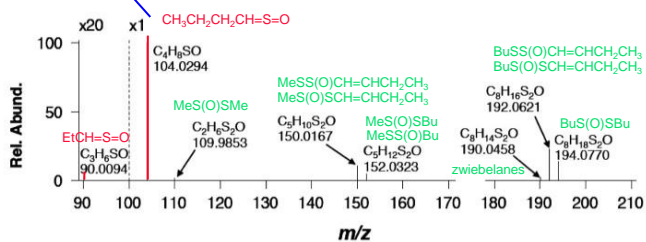
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DART Results

A New Natural Lachrymator: (Z)-Butanethial S-Oxide



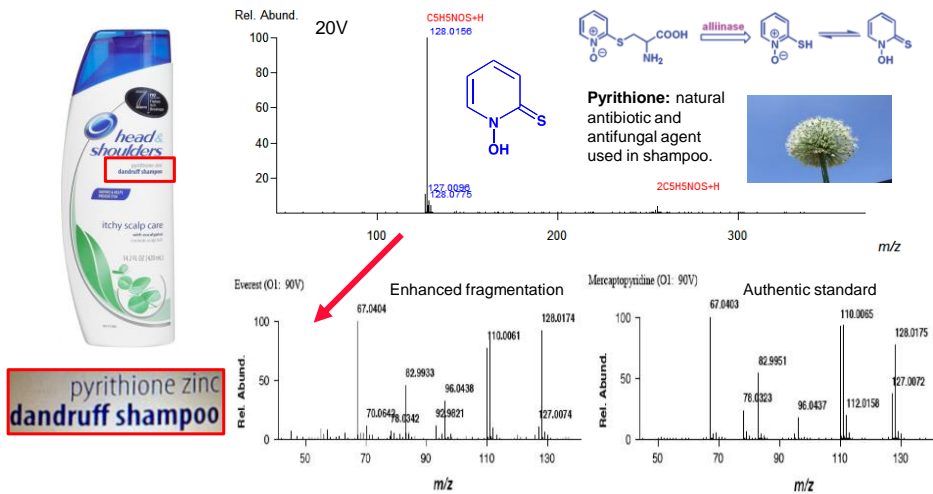
Allium siculum



Block et al., J. Agric. Food Chem. 2010, 58, 1121

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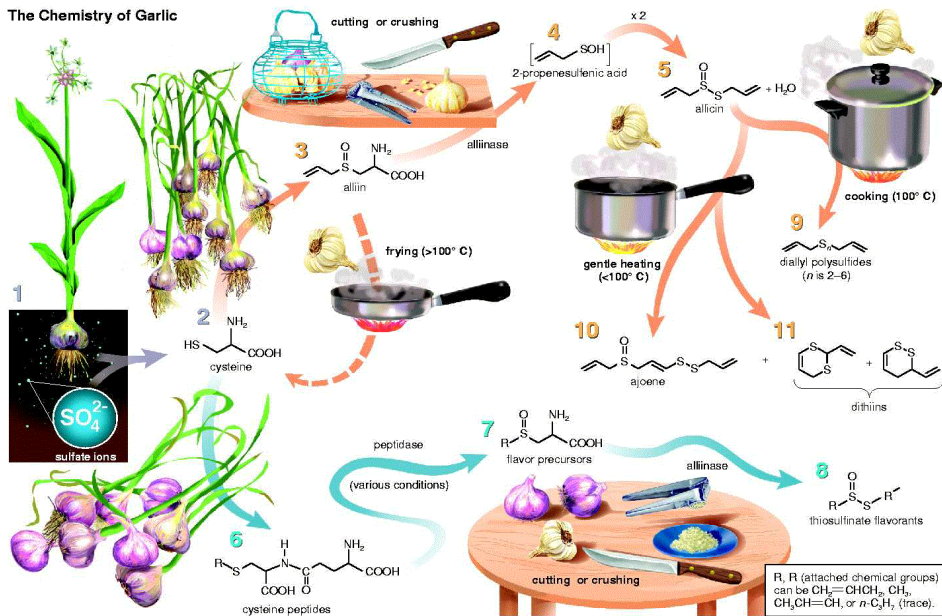
Allium stipitatum: DART-MS Analysis Reveals that Major Volatile is a known Antibacterial and Antifungal Agent!



Block et al., Phosphorus, Sulfur, Silicon Rel. Elements, 2011, 186, 1085

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To Summarize the Chemistry:



Encyclopedia Britannica 1998 Medical and Health Annual, 1997, 222-229

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Acknowledgments:

My outstanding coworkers & the National Science Foundation

Selected References:

Eric Block, "The Chemistry of Garlic and Onions," *Scientific American* 1985, 252, 114-119.

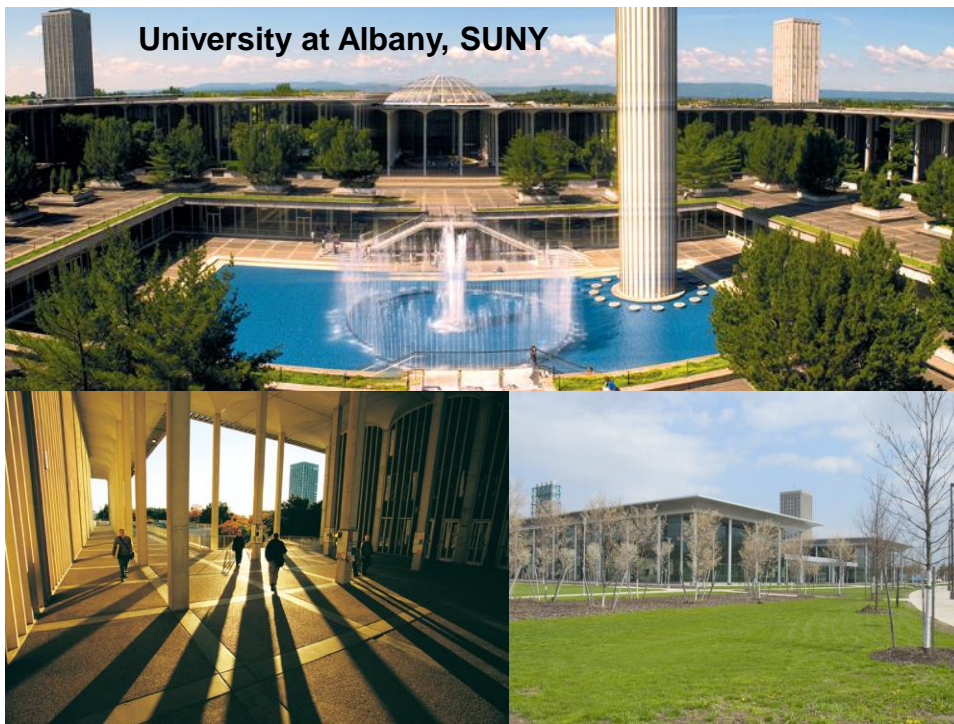
Eric Block, "The Organosulfur Chemistry of the Genus *Allium* - Implications for Organic Sulfur Chemistry," *Angew. Chem. Int. Ed. Engl.* 1992, 31, 1135-1178.

Eric Block, *Garlic and Other Alliums: The Lore and the Science*, Royal Society of Chemistry, Cambridge, UK, 454 pp., 2010.
http://www.amazon.com/Garlic-Other-Alliums-Lore-Science/dp/1849731802/ref=sr_1_1?ie=UTF8&s=books&qid=1284407108&sr=1-1

Eric Block, "Fifty Years of Smelling Sulfur," *Journal of Sulfur Chemistry* 2013, 34, 158-207.

Alan J. Slusarenko et al., "Allicin: Chemistry and Biological Properties", *Molecules* 2014, 19, 12591-12618.

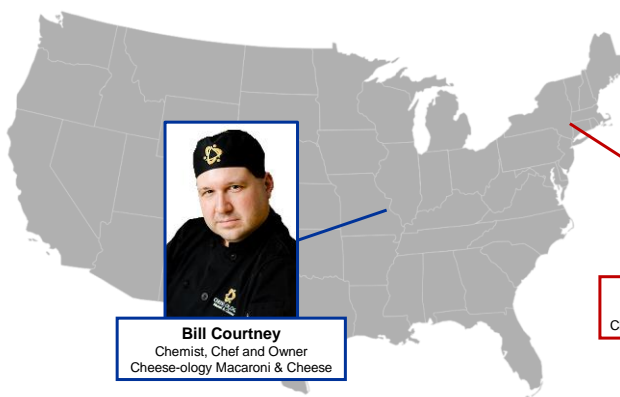
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University at Albany, SUNY



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Bill Courtney
Chemist, Chef and Owner
Cheese-ology Macaroni & Cheese

Dr. Eric Block
Author and Professor of
Chemistry, University at Albany

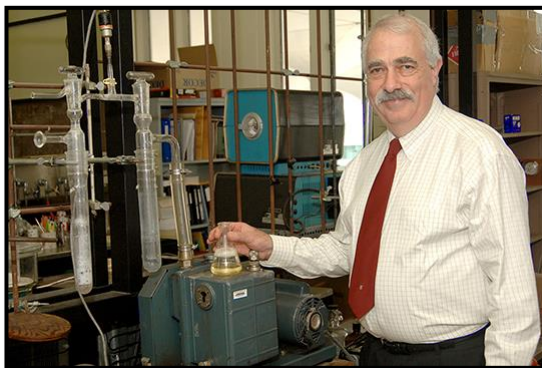
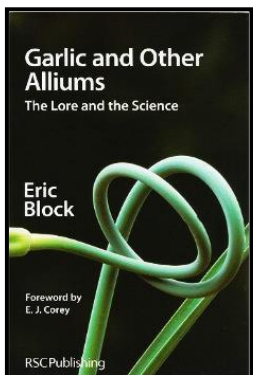
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Dr. Tara Henriksen, Senior Chemical Engineer and Certified Fire and Explosion Investigator, CASE Forensics Corp.



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Dr. Richard Willke, Health Economist, Pfizer
Dr. Robert Koch, Partner and IP Specialist, Milbank

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Bill Courtney
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Dr. Eric Block
Author and Professor of
Chemistry, University at Albany

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Thursday, September 18, 2014

“Tragic Chemical Accidents: Combustible Dust Hazards”

Dr. Tara Henriksen, Senior Chemical Engineer and Certified Fire and Explosion Investigator, CASE Forensics Corp.



Thursday, September 25, 2014

“Pharmacoeconomics and IP Strategies in Drug Development” Session 7

Dr. Richard Willke, Health Economist, Pfizer
Dr. Robert Koch, Partner and IP Specialist, Milbank

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