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**Upcoming ACS Webinars**

[Image]

**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.

[Image]

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Next in the ACS Fellows Program Series!

Thursday, November 13, 2014

Contact ACS Webinars ® at acswebinars@acs.org
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
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

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

The genus Allium includes a total of 600-750 species
The Diversity of Garlic Cultivars

Ajo Rojo (Creole)  German Giant (Rocambole)  Thermadrone (Asiatic)

Italian Purple (Artichoke)  Purple Glazer (Glazed Purple Stripe)  Slovenian (Rocambole)

Source: www.gourmetgarlicgardens.com/varietys

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

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

Readying plant specimens for transport from Russian Asia.
Transporting plant specimens from Russian Asia.

What is known about the role of garlic and other alliums in the arts and literature?
Mrs. Loudon 1841

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

Alliums in Ancient Egypt

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)

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.
Onions in Painting: Vincent van Gogh

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

Numbers 11:4-6
Onion Domes in Architecture:  
Saint Basil’s Cathedral, Moscow

Garlic Domes in Architecture:  
Casa Batlló, Antoni Gaudí, Barcelona
What do we know about the cultivation and sale of garlic and onions?

**Audience Survey Question**

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

- Egypt
- China
- USA
- Liechtenstein
- Japan
800,000 Acres of Garlic:
Shandong, China

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

**Targets for Garlic Sulfur Compounds**

- Poultry red mite
- Cabbage root fly
- Slugs
- Rice blast fungus
- Carrot root fly
- Fungus and mould
- Mosquitoes
- Antimicrobial

Garlic Oil as a Green Nematicide

Far left: carrots showing multiple root nematode damage. Mid left: avoidance index of two populations of nematode C. elegens 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

Annex 1 listing, EU directive 91/414; UK PSD approved
What do we know about the **health benefits** of garlic?

**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 μL of 280 μg Allicin in 20 μL)(left) and (b) Ampicillin (0-100 μg)(right)

Face Mask for Inhalation of Garlic Oil for Treatment of Tuberculosis

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

Garlic Treatment: Burns to Feet and Elbow

(Don’t try this at home!)

Does Garlic Reduce Cholesterol Levels?

Garlic Study: Design

N = 60/group (hyperlipidemic)

<table>
<thead>
<tr>
<th>Daily Tablets</th>
<th>Daily Sandwiches WITH or WITHOUT Garlic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Placebo</td>
<td>WITH</td>
</tr>
<tr>
<td>Garlicin</td>
<td>WITHOUT</td>
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<tr>
<td>Kyolic</td>
<td>WITHOUT</td>
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<td>Placebo</td>
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Fresh Garlic

Garlicin (garlic powder)

Kyolic (aged garlic extract)

Placebo

Lipids

3-Year trial funded by NIH / NCCAM
Stanford Center for Research in Disease Prevention: C.D. Gardner, L. Lawson, E. Block

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


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.
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”

What is known about the **organosulfur chemistry** of garlic and onion or “Allium chemistry”?
What chemical species is named after garlic?

- allyl
- gallium
- stinkium
- aluminium
- garlicium chloride

**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
Allium Chemistry

**Alliinase Enzymes**

- **Precursors** → **Intermediates** → **Primary Flavorants**

- Distillates (Headspace volatiles)

Secondary Products

---

Garlic Chemistry

**Cysteine sulfoxide precursor** (allin)

- (allyl = 2-propenyl)

- **Alliinase**

  - **Sulfenic acid intermediate**

  - **X2 (- H2O)**

  - steps

  - **NH3 + pyruvate**

  - polysulfides

  - ajoene [Block et al. 1984]

---

Chester J. Cavallito [1915-2010]
Sterling Winthrop Co., 1945
Onion Chemistry

cysteine sulfoxide precursor (isoalliin)

alliinase

(1-propenyl)

sulfenic acid intermediate

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

**Elephant Garlic (A. ampeloprasum)** but not Garlic

Produces LF as well as Allicin

Block, Dane, Thomas, Cody, J. Agric. Food Chem. 2010, 58, 4617
Allium siculum (Nectaroscordum siculum) used as a seasoning in Bulgaria

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

Block et al., J. Agric. Food Chem. 2010, 58, 1121
**Allium stipitatum:** DART-MS Analysis Reveals that Major Volatile is a known Antibacterial and Antifungal Agent!

*Pyritihione:* natural antibiotic and antifungal agent used in shampoo.

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

---

**To Summarize the Chemistry:**

*Encyclopedia Britannica 1998 Medical and Health Annual, 1997, 222-229*
My outstanding coworkers & the National Science Foundation

Selected References:


University at Albany, SUNY

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