

## THE CHEMISTRY OF GARLIC HEALTH BENEFITS

Garlic has been viewed for its health benefits for thousands of years, and recently science has begun to show why.

By RICHARD A. PASSWATER, Ph.D.

The following interview was conducted by WholeFoods science editor Dr. Richard Passwater with professor Eric Block, Ph.D., one of the foremost garlic researchers. Dr. Block has conducted extensive research on the sulfur compounds of garlic at the State University of New York at Albany. In 25 years of studying sulfur-containing compounds, he has authored more than 120 scientific articles. He received his Ph.D. from Harvard University with Nobel Laureate E.J. Corey.

**Passwater:** *We have known of garlic's health benefits for thousands of years, but recently I've noticed an increased interest in garlic research. Now that you and other scientists have elucidated the key aspects of the chemistry of garlic that help explain how garlic actually brings about these benefits, garlic is beginning to receive wider attention from nutritionists. Besides "folklore," what suggestions or evidence have we had that garlic has major health benefits?*

**Block:** Epidemiological and medical studies suggest that individuals regularly consuming garlic show a lower incidence of stomach cancer, have longer blood clotting times and show lower blood lipid levels (which indirectly translates into reduced risk of stroke and cardiovascular disease).

**Passwater:** *Do these people generally eat raw, cooked garlic or both?*

**Block:** Garlic is generally processed in some way, such as by cooking, or is cut and mixed with salad oil. Some people do eat garlic raw although this is not recommended. Raw garlic can be very irritating and could injure the digestive tract.

**Passwater:** *Sulfur compounds tend to be very fragile and volatile. Do many of the beneficial garlic sulfur compounds survive cooking?*

**Block:** Some do and some don't. In point of fact, cooking can convert the more fragile sulfur compounds into other sulfur compounds which are also beneficial and at the same time are a bit more robust.

**Passwater:** *What sulfur compounds are present in garlic and what happens to them?*

**Block:** Sulfur compounds from fresh garlic can be divided into five categories:

The first is stable, odorless derivatives of the natural, sulfur-rich amino acid known as cysteine, found in unbroken garlic cloves and bulbs. Alliin (pronounced al-lean) is an example of this type of compound.

Next are compounds with a very brief existence called intermediates (the chemical equivalents of shooting stars), formed when we cut, crush or chop garlic cloves thereby freeing an enzyme (allinase is the name of the garlic enzyme), which acts on the cysteine compounds such as alliin. We know little about the intermediates for they disappear in a fraction of a second after being formed and can never be stored even at low temperatures.

The third category of sulfur compounds are the isolable, but nonetheless unstable and reactive compounds having a typical fresh garlic aroma and taste, formed by very rapid joining together intermediates and found both in garlic juice as well as in the air above chopped garlic. Allicin, (pronounced "alice-in") is a well known example of compounds of this type. Actually our recent research has shown that as many as nine "chemical cousins" of allicin are also formed when garlic is cut. These other compounds also have a typical garlic aroma and taste. While allicin and its "cousins" can be prepared in pure form and studied in the research laboratory, they are termed "unstable compounds" meaning that at room temperature they have a very limited shelf life (a few hours) and cannot be stored without using special low temperature refrigerators.

More stable products are formed when alliin and its "cousins" stand at room temperature for a few hours or days.

A good example of this situation is macerate of garlic, a product formed when garlic is chopped ("macerated") with salad oil or other edible oils. Macerate of garlic is a rich source of "naturally-formed" garlic-derived compounds having the scientific names ajoene, methyl ajoene, and dithiins. These products are stable enough to be stored at room temperature for more than a year, for example when dissolved in an edible oil.

The fifth category is materials prepared by heating garlic in boiling water and condensing (collecting) the steam as it becomes a vapor, a technique known as steam distillation. The product is termed the distilled oil of garlic. The scientific name for the major component of distilled oil of garlic is diallyl disulfide. It has a strong, slightly medicinal, "artificial" smell of garlic. Distilled garlic oil is used as a food flavoring agent.

To summarize, when we cut or crush fresh garlic, we release an enzyme called allinase, which rapidly converts odorless alliin to allicin, the latter having the typical odor and taste of fresh garlic. Allicin is unstable and rapidly reverts to ajoene (pronounced ah-hoe-ene) and dithiins (pronounced di-thigh-eins) in the presence of edible oils (e.g. macerates) or to diallyl disulfide on standing or heating in water.

**Passwater:** *Are you saying that it is not the alliin and allicin themselves that are important, but compounds that are formed from these compounds, either in the body or by certain types of cooking?*

**Block:** If by "important" you mean "having a positive health benefit" the answer to that question is still actively being sought by researchers. There seems to be health benefits associated with most of the sulfur-rich components of garlic following its normal use in cooking and consumption. For example, I've already mentioned that ajoene and dithiins are naturally formed when garlic is macerated with various edible food oils.

**Passwater:** *I had seen several recent articles describing the benefits of ajoenes, but I was not familiar with them. In fact, I didn't even remember ever studying "ajoenes," and they didn't seem to fit into standard terminology, so I had to check the Merck Index for details.*

**Block:** Don't feel too bad. I discovered them in 1984 and named them in honor of my collaborators in this research from Venezuela. "Ajo" is the Spanish word for garlic. I'm quite proud that ajoene has been included in the latest edition of the Merck Index. By the way, alliin and allicin are derived from the botanical Latin name for garlic, *Allium sativum*.

**Passwater:** *How many papers have been published about ajoenes since you discovered and named them?*

**Block:** I have seen more than a dozen scientific papers from laboratories around the world dealing with medical benefits of ajoenes. I have also seen quite a few papers dealing with ajoene analysis and occurrence. These latter papers indicate that macerated garlic is the only form of garlic where significant quantities of ajoenes and dithiins have ever been detected.

**Passwater:** *What health benefits do ajoenes provide?*

**Block:** As I said, ajoenes and dithiins are among the most active compounds formed from fresh garlic. Ajoenes have been shown to: possess antithrombotic (anticlotting) activity in human platelet suspensions (1-8); possess antitumor activity (9); display significant antifungal activity, inhibiting the growth of *Aspergillus niger*, *Candida albicans*, *Paracoccidioides-Brasiliensis*, and *Fusarium* species (10-12); inactivate human gastric lipase, a sulfhydryl enzyme involved in the digestion and adsorption of dietary fats (13); function as antioxidants by inhibiting the interactions of leukocytes, which mediate release of superoxide anion (14).

In one interesting study, administration of ajoene to dogs under

extracorporeal circulation (as used in open heart surgery) prevents the thrombocytopenia induced by contact of blood with artificial surfaces. In this same study, ajoene showed excellent activity in preventing loss of platelets and increasing the rate of restoration of platelet clotting activity (1-5).

Exciting advances have also been reported for dithiins as well. For example, a U. S. patent was recently awarded to a scientist at the Los Alamos National Laboratory for the invention of a copolymer involving the same dithiin formed from garlic for an "antithrombogenic and antibiotic composition for use as a coating for artificial prostheses and implants which remain in contact with blood" (15). Thus, basic research on garlic chemistry has led to the development of a new type of plastic in which a stable garlic-derived anticlotting and antibiotic agent provides unique properties of potential use in heart valves, artificial blood vessels and other implant devices.

**Passwater:** *Are the ajoenes and dithiins the only garlic components that are actively being studied for possible protection against heart disease?*

**Block:** As far as I am aware.

**Passwater:** *When we are talking about the health benefits from garlic and garlic's sulfur-containing compounds, is it your view that we are not talking about sulfur-compound nutriture, such as with the sulfur-containing amino acids cysteine or methionine, but with the "herbal" properties of garlic, which are health benefits beyond those of nutrients?*

**Block:** I would like to respond with a qualified yes. In addition to those compounds formed from garlic such as allicin and ajoene, there are various cysteine derivatives from garlic related to alliin containing allyl groups attached to cysteine sulfur, which may also have health benefits. However to be of value, these allylic compounds would have to be present in significant quantities in what is consumed.

**Passwater:** *You mentioned that we get the most beneficial compounds from cooked garlic or garlic prepared with edible oils and not directly from raw garlic - what about garlic supplements?*

**Block:** My basic research through the years has focused on fresh garlic and compounds such as ajoene directly derived from fresh garlic and on the biological activity of pure samples of ajoene and related compounds. I myself have not been involved in the preparation or evaluation of different commercial garlic supplements so I can only answer your question based on what I have read in the open literature.

There are quite a variety of different garlic products on the market. There is certainly a need for independent testing and evaluation of these different products and careful examination of their claims. Some products talk about allicin content, allicin potential or allicin yield. Since there is no way to stabilize allicin itself, any claims concerning actual allicin content in a product cannot be correct. Intact garlic cloves themselves do not contain allicin either, although upon cutting or crushing under ordinary circumstances allicin is formed.

Thus, one can talk about the allicin potential or allicin yield from garlic cloves. If garlic cloves are frozen in dry ice, pulverized with acetone in the absence of water, and the powder is then briefly heated with alcohol, not a trace of allicin can be detected following addition of water because these conditions destroy or "denature" the allinase enzyme, which is required for allicin production.

These very conditions were employed 50 years ago by Chester Cavallito, the discoverer of allicin, to demonstrate that an active enzyme is a requirement for allicin formation. In this particular case, the allicin potential is unfulfilled because the enzyme has been denatured.

With a garlic supplement claiming allicin potential, I would assume one is talking about some type of preparation in which water has been removed from garlic and the resulting product then pulverized and encapsulated. I further assume that when the contents of the capsule are exposed to water, allicin is produced. The critical question is whether or not the required enzyme is destroyed during the actual digestive process at the time when the coating of the capsule dissolves. Just as hot alcohol can denature the sensitive allinase enzyme, so too can the strong acid present in our stomach.

While allicin itself is highly unstable and can only be produced when both the precursor alliin and the enzyme allinase are present under non-denaturing conditions, the situation with ajoene-containing products such as garlic macerates is somewhat different. Since ajoene and dithiins are already present in the macerate, no sensitive enzyme is

required. To the best of my knowledge, the only commercial products which have been unequivocally shown to contain significant quantities of ajoene and dithiins are macerates of garlic.

**Passwater:** *Is there a direct relationship between the amount of beneficial garlic compounds in your system and being able to detect their presence on your breath?*

**Block:** Garlic breath has been a matter of concern since garlic was first cultivated and used as a seasoning thousands of years ago. The fact is that the human nose is extraordinarily sensitive to the very types of sulfur compounds formed when we digest garlic and its derived products such as allicin, ajoene and diallyl disulfide. When the sulfur compounds are digested they are broken down into simpler sulfur compounds, a portion of which enters the bloodstream and is then exhaled from the lungs or eliminated through our pores when we sweat. Since the human nose can detect less than one part of these sulfur compounds in one billion parts of exhaled air, it doesn't require much garlic or garlic compounds to give us garlic breath. It has even been reported that babies born to mothers who consumed garlic prior to giving birth have garlic breath. Not that the babies complain! In fact, other studies suggest that babies actually prefer slightly garlicky mother's milk. If we can assume that it is the sulfur compounds of garlic that are primarily responsible for its health benefit, then it seems illogical to expect benefits, from a product where not a trace of garlic breath can be detected after consumption.

**Passwater:** *What do you see happening with garlic research? What is your next garlic or sulfur chemistry problem to solve?*

**Block:** At the present time the use of garlic in cooking and, in processed form, by the food industry constitutes the largest market for the "stinking rose." There is still a need for better analytical methods to accurately and rapidly measure the amounts of allicin and related compounds in freshly cut garlic and to understand the fate of garlic flavorants under a variety of processing or culinary conditions. At the same time, we need to better understand the biological properties of the various types of sulfur compounds formed from garlic and, in particular, to rigorously establish the effect of these different compounds on human health and in the prevention of disease. Since there is great interest in garlic and its health benefits, I believe we will be seeing significant and exciting progress in all of these areas during the next few years. **WF**

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