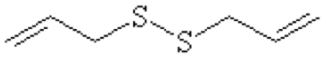
alliums: their curious properties

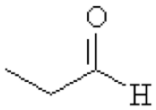
If you peel or chop an onion, often your eyes begin to water. What causes this? It seems obvious - something in the onion causes it. But an uncut, unpeeled onion is not lachrymatory (meaning a substance which causes crying) and has almost no odour. So the substance that causes crying must be produced only upon peeling or chopping. Similiarly in garlic - the distinctive smell of garlic only occurs when the garlic is chopped, peeled or crushed. There is some biochemical mechanism that produces these substances only after peeling or chopping.

Theodor Wertheim, a German chemist was the first to carry out a chemical study of garlic. In 1844 he extracted 'garlic oil' from garlic by steam distillation. He commented on the sulfurous nature of this oil, and named the hydrocarbon group present 'allyl'. This name is still in use today, it describes the group CH_2=CH-CH_2-.

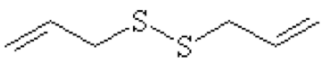
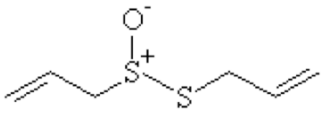
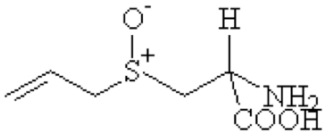
Semmler in 1892 identified a component of the oil as diallyl disulfide:



He also extracted onion oil, and identified it as containing, among other things, propanal:



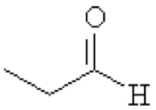
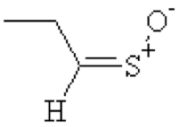
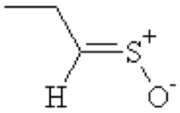
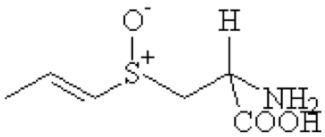
Neither of these chemicals cause the effects described above. What's going on? The substance responsible for the properties must be sufficiently unstable to decay to the above products when subjected to the harsh conditions of steam distillation. Cavallito and others working in the US in 1944 extracted compounds from garlic using gentler conditions than steam distillation. He found that certian compounds predominated under certain conditions:

method of extraction from garlic	compound extracted (click for 3-D!)
steam	 diallyl disulfide
ethanol and water, room temp	 allicin
cold ethanol	 alliin

The substance responsible for the smell of garlic is allicin, and it is formed from alliin when the garlic is cut or crushed. Alliin is an amino acid based on cysteine, and it has 4 stereoisomers (exciting chemical fact! for those who are interested.) Only one isomer is present in garlic.

Onions were investigated in a similiar way by the Finnish Nobel laureate Artturi Virtanen. He applied similiar extraction methods to those used by Cavallito to onions and found the following:

method of extraction from onion	compound extracted (click for 3-D!)

steam	 propanal
freon and water, cold	 syn- lachrymatory factor  anti-lachrymatory factor
cold ethanol	 lachrymatory precursor

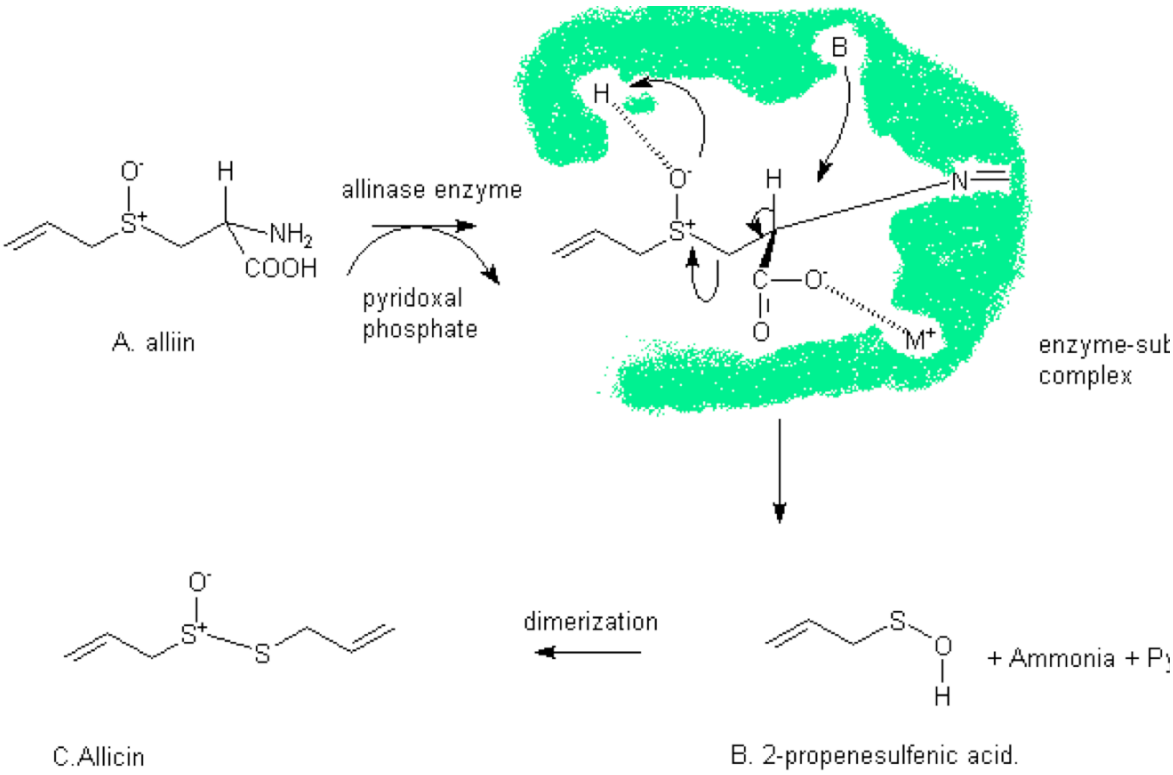
The lachrymatory factor is the compound that causes crying when onions are peeled. It has two forms, termed syn and anti (these names correspond to the different arrangements of the bonds in space). Notice that the lachrymatory precursor differs from alliin only in the position of the carbon-carbon double bond.

Further work has lead to the discovery of the reactions that occur in cut garlic and onions, and the next page will explain....

1. Garlic.

The biochemical reactions that occur in chopped garlic were first probed in 1948 by Stoll and Seebeck of the Sandoz chemical company. They explained why the formation of allicin occurs only on cutting by a enzyme catalysed mechanism. When garlic is chopped or crushed, the garlic tissue is damaged and the precursor, alliin comes into contact with the enzyme allinase. It was later discovered that another biological compound, pyridoxal phosphate, must also be present. The enzyme catalyses the decay of alliin to an unstable intermediate, 2-propenesulfenic acid. This dimerizes to give allicin. Allicin is also unstable and reacts with other compounds present to give many products. More on these products on the next page.

Pathway for the formation of allicin from alliin:

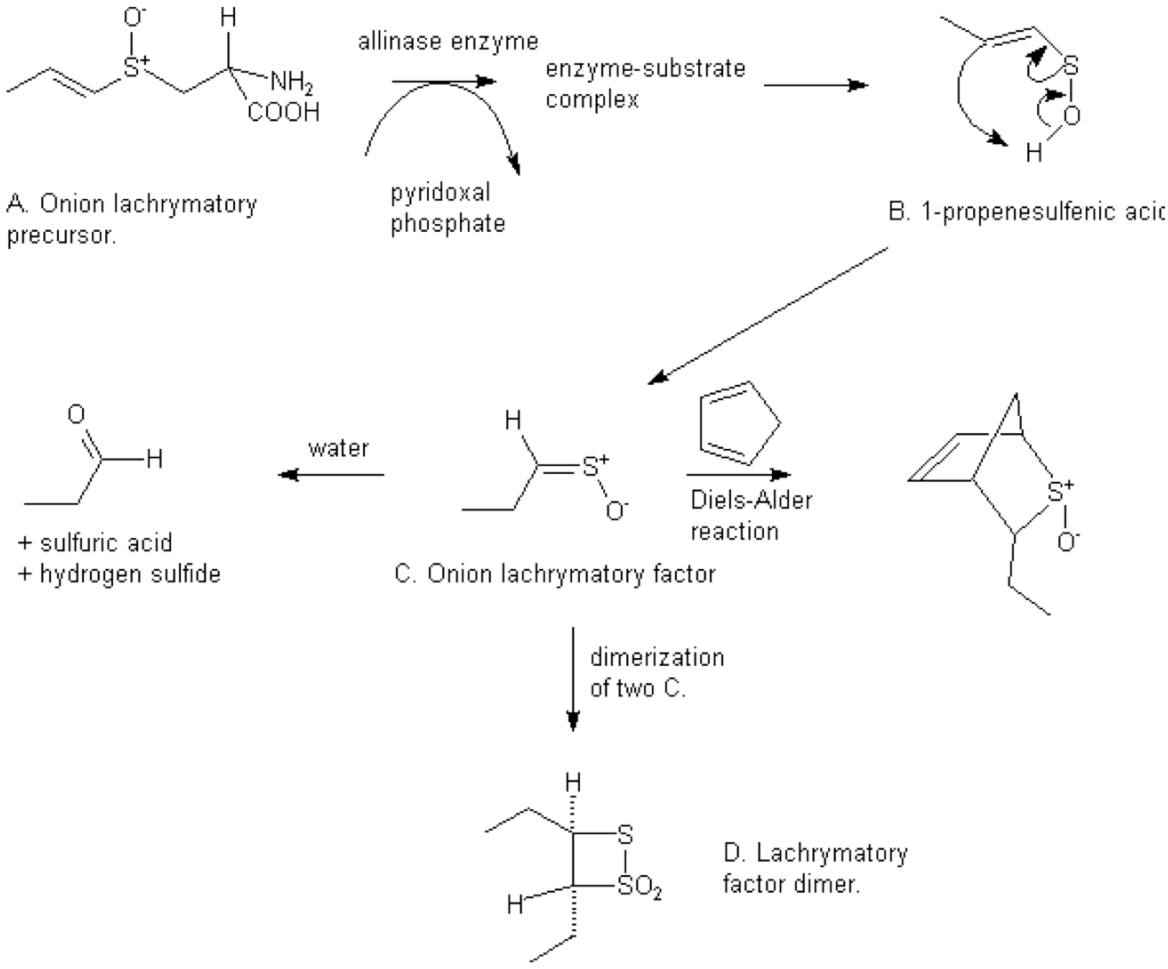


2. Onion.

The structure of the lachrymatory precursor in onion is very similiar to that of alliin, so one would expect its reactions to be very similiar. This is true up to a point; the lachrymatory precursor is broken down by allinase to give a 1-propenesulfenic acid. The double bond is in a different place to that formed from garlic, and this double bond allows the sulfenic acid to isomerize to give the lachrymatory factor - the compound that causes tears when chopping onions. This compound has two isomers, syn and anti. Both are formed but the syn compound is formed preferentially. Like allicin it is unstable. It is hydrolysed to give propanal and can dimerize. It can also undergo Diels-Alder cycloaddition with cyclopentadiene.

Pathway for the formation of lachrymatory factor from precursor; and some possible reactions of the lachrymatory factor:

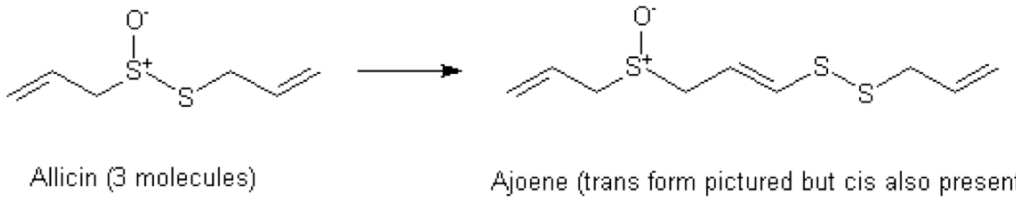
The formation of onion lachrymatory factor from its precursor, and its decay.

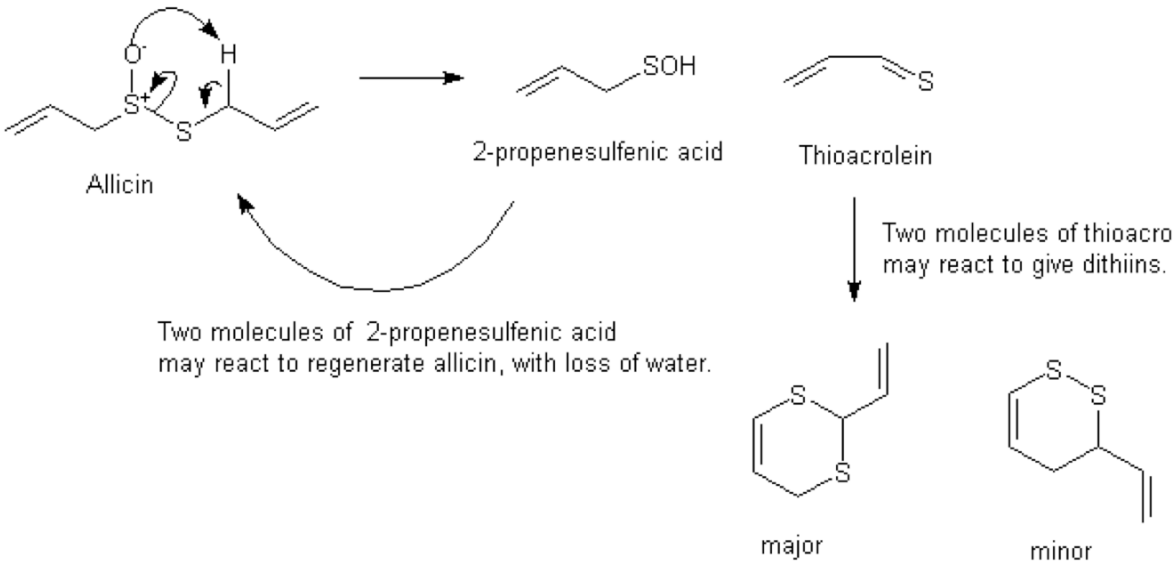


The discomfort sometimes associated with peeling onions can be reduced by two methods. Chilling the onion reduces the volatility of the lachrymatory factor, and peeling under running water dissolves the lachrymatory factor before it can have an effect.

Allicin is a powerful antibiotic. It will kill e. coli, streptococcus and others, and is one fiftieth as powerful as penicillin. Garlic has often been used as antithrombotic, and an epidemiological study carried out by Sainini at the University of Poona seems to confirm this. The beneficial properties of garlic have been attributed to allicin itself, and the products that form upon its decay. The diagram below explains a few of these reactions.

Reactions of allicin.





Allicin reacts with itself to give ajoene (from *ajo* spanish for garlic.) It is an antithrombotic agent at least as potent as aspirin. It inhibits the formation of platelets by binding to the fibrinogen receptor, thus rendering it unable to bind to other fibrinogen receptors. Allicin may also decay to give 2-propenesulfenic acid and thioacrolein. Allicin may be regenerated from 2-propenesulfenic acid. Thioacrolein can react with another molecule of thioacrolein via a Diels-Alder reaction to give two dithiins. These are also mildly antithrombitic. It is worth noting that some'garlic pills' do not contain ajoene or many other beneficial compounds. The method of manufacture of these garlic pills uses steam distillation, and this can break down some of the beneficial compounds. So, if you want the health benefits of garlic, you should really eat proper garlic!