The Universal Hotness, Part 1: Allyl Isothiocyanate[a]

Chemistry and application in flavor

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Allyl isothiocyanate (FEMA# 2034, CAS# 57-06-7; mustard oil) **(F-1)** is a colorless oil that is responsible for the pungent taste of mustard, horseradish and wasabi. It is found in mustard, horseradish, cabbage, sauerkraut, milk, beans, cauliflower and Brussels sprouts. It has a stinging, sulfuric, mustard odor and pungent, sharp, characteristic mustardlike flavor; on dilution it possesses a vegetable note.[b]

Allyl isothiocyanate is naturally produced by hydrolysis of natural rhizome thioglucosides, which are conjugates of the sugar glucose and sulfur-containing organic compounds. This hydrolysis is catalyzed by the enzyme myrosinase, which is capable of hydrolyzing glucosinolates. The hydrolysis occurs when the enzyme is released on cell rupture caused by the maceration of the plant's rhizome. An example in which sinigrin (CAS# 3952-98-5) is hydrolyzed into allyl isothiocyanate and its isomer, 1-cyano-2,3-epithiopropane (CAS# 58130-93-1) is shown **(F-2)**.[1]

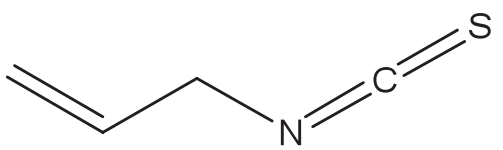
The unique flavor of wasabi, for example, is a result of complex chemical mixtures from the broken cells of the rhizome, including those resulting from the hydrolysis—glucose and other methylthioalkyl isothiocyanates (**F-3**). Additional examples of isothiocyanates used in flavors can be seen in **F-4**.

Variations of western mustards (*Brassica nigra*) come from England, the Netherlands, France, Poland, Sweden, Russia, the United States and Germany. Horseradish (*Armoracia rusticana*) is also used in the United States, but mostly in Central and Eastern Europe. Wasabi (*Wasabia japonica*), of course, is a key flavor in Japan. Allyl isothiocyanate can be applied for mustard-type flavoring and vegetable formulations of cauliflower and cabbage.

Able to be produced commercially by a reaction of allyl chloride and potassium thiocyanate **(F-5)**, allyl isothiocyanate made this way is sometimes known as synthetic mustard oil.

Natural allyl isothiocyanate (mustard oil) is mostly liberated by dry distillation of the seeds. The product obtained in this method is known as volatile oil of mustard and is usually around 92% pure. The material contains other isomers, such as allyl thiocyanate (CAS# 764-49-8) **(F-6)**, which is most likely an artifact caused by partial isomerization of allyl isothiocyanate under the condition of isolation and/or analysis.[2]

Allyl isothiocyanate **F-1**



Physical Data for Natural Allyl Isothiocyanate

Appearance: Colorless to pale yellow liquid

Molecular weight: 99.15

Molecular formula: C_4H_5NS

Refractive index (n^{20}/D): 1.515–1.540

Specific gravity ($D^{20/20}$): 1.005–1.035

Purity (GC area): 92% (min.) (total isomers)

Flash point: 46°C

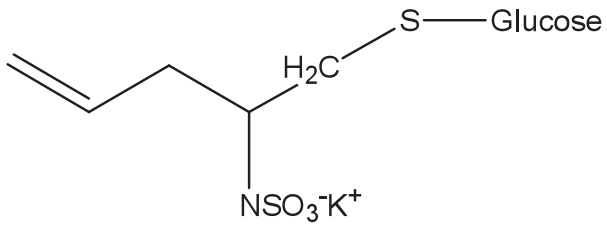
Log P: 2.15

[a]Part 2 will deal with black pepper hotness, and Part 3 with capsicum, ginger and curcumin, with Sichuan peppercorn.

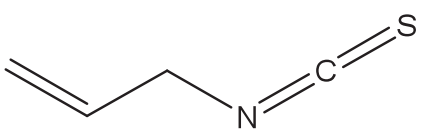
[b]Most of the information on organoleptic properties and uses are taken from FRM 2001 Database, Boelens Aroma Chemicals Information Services, The Netherlands.

Sinigrin hydrolyzed into allyl isothiocyanate and 1-cyano-2,3-epithiopropane

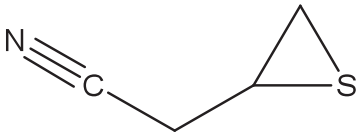
F-2



Sinigrin



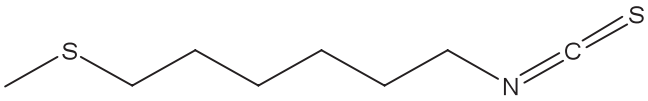
Allyl isothiocyanate



1-Cyano-2,3-epithiopropane

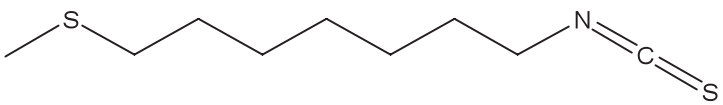
Methylthioalkyl isothiocyanates

F-3



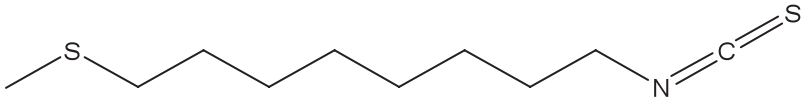
6-methylthiohexyl isothiocyanate

(FEMA# 4415, CAS# 4430-39-1)



7-methylthioheptyl isothiocyanate

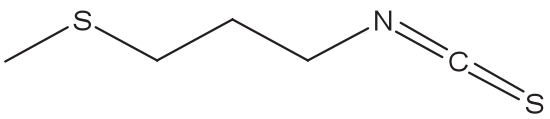
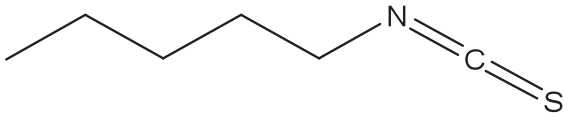
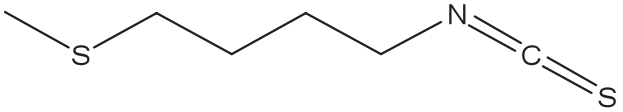
(CAS# 4430-38-0)



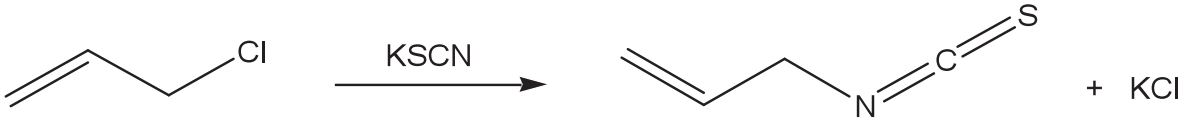
8-methylthiooctyl isothiocyanate

(CAS# 4430-41-5)

Examples of isothiocyanates and uses F-4

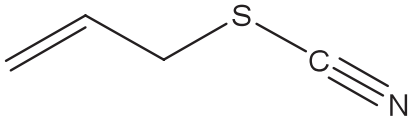
Structure/Name/FEMA# and CAS#	Organoleptic description
 3-Methylthiopropyl isothiocyanate FEMA# 3312, CAS# 505-79-3	Rooty, pungent, vegetative, sulfurous and horseradishlike; earthy and metallic nuances
 Amyl isothiocyanate FEMA# 4417, CAS# 629-12-9	Green
 4-Methylthiobutyl isothiocyanate FEMA# 4414, CAS#4430-36-8	Cabbage, radish

Allyl isothiocyanate as a reaction of allyl chloride and potassium thiocyanate F-5



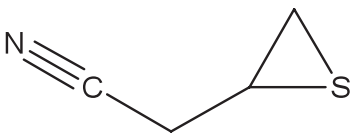
Allyl chloride — Allyl isothiocyanate

Allyl thiocyanate F-6



Allyl thiocyanate

1-Cyano-2,3-epithiopropane F-7



1-Cyano-2,3-epithiopropane

Cabbage seeds contain several glucosinolates and, on autolysis, produce, notably, 1-cyano-2,3-epithiopropane (CAS# 58130-93-1) **(F-7)**, which is another isomer of allyl isothiocyanate.[3]

The pungent feeling caused by allyl isothiocyanate is caused by an activation of the heat thermo- and chemo-sensitive transient receptor potential (TRP) ion channels including TRPA1. These receptors mediate a variety of sensations such as pain, hotness, warmth or coldness, different kinds of tastes, pressure, and vision nociceptors, which are sensory receptors that respond to potentially damaging stimuli by sending nerve signals to the spinal cord and brain. Nociceptors usually cause the perception of pain.

TRPA1 is an ion channel located on the plasma membrane of many human and animal cells. This ion channel is best known as a sensor for environmental irritants, pain, cold and stress. Recent studies indicate TRPA1 is activated by a number reactive compound, with one of them being allyl isothiocyanate.[4]

Nociceptors are sensory neurons that are found in any area of the body that can sense pain either externally or internally. External examples are in tissues such as skin (cutaneous nociceptors), cornea and mucosa. Internal nociceptors are in a variety of organs, such as the muscle, joint, bladder and gut, and continuing along the digestive tract. The cell bodies of these neurons are located in either the dorsal root ganglia or the trigeminal ganglia. The trigeminal ganglia are specialized nerves for the face, whereas the dorsal root ganglia associate with the rest of the body. The axons extend into the peripheral nervous system and terminate in branches to form receptive fields.[5]

References

1. KH Kyung, HP Fleming, CT Young and CA Haney, *J Food Sci*, **60**(1), 157 (1995).
2. GP Slater, *Chromatographia*, **34**(9–10), 461–467 (1992).
3. N Kaoullaa, A J MacLeoda and V Gil, Investigation of *Brassica oleracea* and *Nasturtium officinale* seeds for the presence of epithiospecifier protein. *Phytochemistry*, **19**(6), 1053–1056 (1980).
4. PG Baraldi, D Preti, S Materazzi and P Geppetti, Transient receptor potential ankyrin 1 (TRPA1) channel as emerging target for novel analgesics and anti-inflammatory agents. *J. Med. Chem.*, **53**(14), 5085–5107 (2010).
5. *Principles of Neural Science*, Edits, TM Jessell, ER Kandel and JH Schwartz, 472–479, Appleton & Lange, Norwalk, Connecticut, (1991).